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DEFORMATION BANDS IN THERMOSET POLYMERS

Carl Levi Ludwig

DEFORMATION BANDS IN
THERMOSET POLYMERS

BY

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LIEUTENANT, UNITED STATES NAVY

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(1964)

Submitted in partial fulfillment
of the requirements for the degree of
Naval Engineer
and for the degree of
Master of Science
in
Naval Architecture and Marine Engineering
at the
Massachusetts Institute of Technology
June, 1970

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ABSTRACT

DEFORMATION BANDS IN THERMOSET POLYMERS

by

CARL LEVI LUDWIG

Submitted to the Department of Naval Architecture and Marine Engineering on May 21, 1970, in partial fulfillment of the requirements for the Master of Science Degree in Naval Architecture and Marine Engineering and the Professional Degree, Naval Engineer.

Thermosetting resins are inherently brittle, but can be toughened considerably by adding rubber particles. This toughening is due to large localized deformations known as crazes and shear bands. The compression test results indicate the shear bands are similar to those formed in thermoplastics. Shear strains of 60% were measured in the bands. The angle of band propagation was usually less than 45°. The bands were generally diffuse in nature, i.e. the yield zone consisted of several shear bands. The stress for band initiation varied directly with the inverse of temperature for the rubber modified and unmodified thermoset tested.

Polystyrene, epoxy and modified epoxy specimens were annealed at temperatures slightly above their glass transition temperatures. No residual strain was apparent by photoelastic techniques, but upon retesting a decrease in both microscopic initiation and the maximum stress was observed. These results indicate the mechanism of shear band initiation may be the parting of covalent bonds in the molecular chain.

The results from the rubber modified epoxy tests qualitatively indicate the presence of a compressive stress due to the difference in the thermal coefficients of expansion. However, quantitative studies could not confirm a rubber particle produced only a compressive stress, provided only a stress concentration, or did both in any consistent manner.

THESIS SUPERVISOR: F. J. MCGARRY

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I. INTRODUCTION

Thermosetting resins are inherently brittle, but considerable toughening is possible by introducing a fine dispersion of rubber particles into a thermoset matrix. Sultan and McGarry[1] have shown the degree of toughness depends upon the size of the second phase particles, the curing temperature, the bonding between the two phases, the molecular weight of the elastomer and its concentration.

This toughening is a result of plastic flow which is probably due to large localized deformations known as crazes and deformation or shear bands. Kambour[2] has found crazes to be deformed roughly 50 percent and Godrick[3] found shear strain in deformation bands to be in the order of unity. Crazes occur in a direction perpendicular to the principal tensile stress axis while the deformation bands propagate in a plane nearly parallel to the plane of maximum shear stress. The deformation bands are similar in appearance to slip bands (Luders' bands) in metals. Newman and Wolock[4] observed the relation between the appearance of crazes and flow lines while loading tensile specimens of polymethyl methacrylate (PMMA). Of a number of specimens observed by Newman and Wolock only three exhibited flow lines. Two of these three

specimens broke at strains of approximately 20%. The third specimen broke at the usual average value which is about 9 per cent. These specimens crazed at strains of approximately 3 per cent as observed in previous tests. The flow lines were first observed at strains of 8 to 10 per cent. The flow lines clearly originated at the ends of crazes and they did not observe craze growth after the appearance of the flow markings. Similar flow lines were observed on the surface of a biaxially stretched plastic sheet that had been stressed to failure without crazing. The nuclei for shear band formation consisted of bits of adhesive from the masking paper.

Ender and Andrews[5] studied similar craze and shear band (flow line) phenomena in Polystyrene. Their results indicate a critical stress is required for the formation or propagation of shear bands. Godrick[3] found the local stress for band initiation to be temperature dependent and the bands initiate when the load-deflection curve deviates from linear.

Polystyrene is a glassy, amorphous thermoplastic at room temperature and below. In tests of other thermoplastics, Godrick[3] and Whitney[6] found that only polyvinyl chloride did not develop some type of shear band. Godrick also tested some lightly crosslinked

(irradiated) polystyrene and the bands developed similar to those in the amorphous polystyrene, but the band initiation stress and the yield stress were increased slightly. The degree of crosslinking was not extensive and it is known that polymer behavior is not influenced very significantly in the glassy region by small amounts of crosslinking. Only if the crosslinking is quite extensive does a marked change occur in mechanical behavior[7,8].

This experimental study investigates the formation of deformation bands in a thermoset polymer and in particular investigates the effects of an elastomeric second phase, such as rubber particles, on deformation band formation.

II. EXPERIMENTAL TECHNIQUE

A. Materials Investigated

The material extensively studied was an epoxy resin, EPON 828*, an epichlorhydrin/bisphenol A product with an epoxide equivalent of 185-205, which is considered to be a representative polymer of its type. Polymerization of the resin was obtained by adding 5 pph by weight of Curing Agent D*, the tri-2-ethylhexanoate salt of DMP-30*. A few tests were conducted on a highly cross-linked epoxy resin, ERLA 4617**, bis (2,3 epoxycyelopentyl ether) which was hardened by adding 5 pph by weight of metaphenylene diamine. Initially, a few tests were conducted on polystyrene.

The second phase elastomer particles were random copolymers of acrylonitrile and butadiene***. Two particle sizes of the Hycar type CBTN were used to modify the EPON 828. Hycar CBTNX was used to modify the ERLA 4617. The rubber modified materials consisted of 10 pph by weight of the respective elastomer.

---

* Mfd. by the Shell Chemical Co., New York, N.Y.

** Mfd. by the Union Carbide Corp., New York, N.Y.

*** Hycar Elastomers, B. F. Goodrich Chemical Co., Cleveland, Ohio.

B. Compression Specimens

1. Specimen Preparation

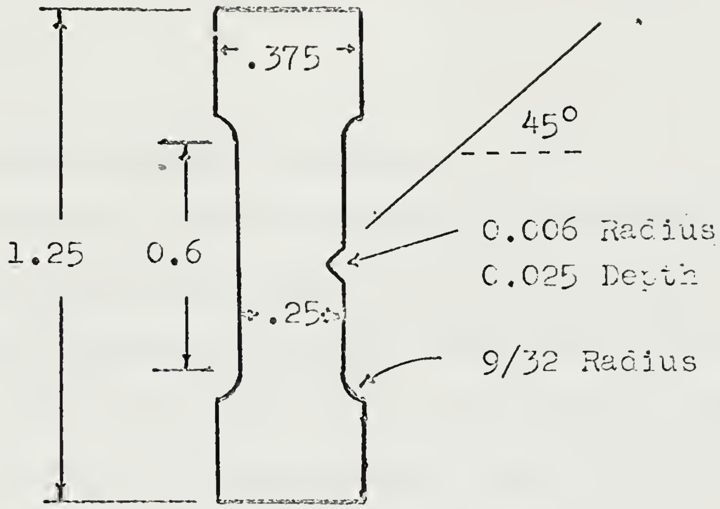
The EPON 828 and modified EPON 828 plates were cast in a mold of two 12" by 12" glass plates separated approximately ½ inch by a rubber gasket. Two curing methods were used. The standard one was to cure at 120°C for two hours. The low temperature method was to cure at 74°C for four hours. The plate was then cut into ½ inch strips on a band saw and the specimens were milled to the desired geometry. Initially, the specimens were pollished by standard metallographic techniques. Later it was found more efficient to mask the cast plates with masking tape. The tape preserved the smooth finish as the paper mask does on the commercially available PMMA or polystyrene sheets. The preparation procedure is detailed in Appendix C.

The polystyrene specimens were milled from a ¼ inch thick commerical sheet purchased from a plastic supply house. The modified and unmodified ERLA 4617 specimens were milled from plates prepared by Laible[9].

2. Specimen Geometry

Figure 1 shows some of the specimens which were investigated. Several compressive tests were conducted on the single notched specimens but buckling and bending were difficult to control. It appeared

(a) A single notched, a double notched, a holed and a control specimen.



(b) Specimen size and notch details. All dimensions are in inches.

FIGURE 1. COMPRESSION SPECIMENS.

that buckling occured just after the shear bands were visible. The double notch solved the bending problem, but the specimen would still buckle. The overall length of the specimen was decreased from 1.375 to 1.25 inches and the gage length from 0.7 to 0.6 inches, but the single notched specimens would still bend and buckle, and the double notched would occasionally buckle. Consequently, the center hole specimen was used for most of the remaining tests. The stress concentration factor was reduced from 3.3[10] for the single notch to 2.35[11] for the holed specimen, but no buckling occured at the macroscopic band initiation stress. Later it was found that no bending or buckling occurs in any of the above specimens at the microscopic band initiation stress.

3. Specimen Identification

All specimens were designated by an alphabetical prefix, a three or four digit number and a numerical suffix. The alphabetical prefix identifies the material, the number identifies the cure, the geometry, and the consecutive number of the specimen. The suffix was used only if the specimen had been annealed and retested. In the example $L_1L_2L_3$ $N_1N_2N_3N_4$-N_5, the first letter, L_1, indicates the basic material, L_2 and L_3 identify the modifying elastomer particle, N_1 indicates the type

of cure, N_2 identifies the specimen geometry, N_3 and N_4 indicate the number of the specimen and N_5 indicates the number of retests. The materials and their identifying codes are as follows:

B	Bakelite, ERLA 4617
BRX	Bakelite, ERLA 4617 modified with 10% Hycar CBTNX
E	EPON 828
ERL	EPON 828 modified with 10% Hycar CBTN, Lot R-146, Ephr 0.034, Br Visi @ 27°C was 475,00.
ERS	EPON 828 modified with 10% Hycar CBTN, Lot R-151, Ephr 0.05, Br Visi @ 27°C was 315,000.
P	Polystyrene

The cure is identified by N_1, which is zero (left blank) for the standard cure at 120°C and is 1 for the low temperature cure at 74°C. The value of N_2 indicates the specimen geometry as follows:

xoxx	Single Notch
x5xx	Double Notch
x6xx	Center Hole
x8xx	Control (no stress concentration factor)

C. Testing Methods

1. Compression Tests

Compression tests were performed with an Instron Testing Machine. Initially, one end was placed on a ball bearing pivot to allow for minor milling discrepancies. However, the specimen's initial location was critical and contributed to buckling. Subsequently, the specimen was tested between two parallel faces. Repeated tests after changing to the holed specimen indicated no significant error from the milling inaccuracies. Most tests were conducted at the crosshead rate of .05 in./min. and room temperature (23.5°C).

2. Band Initiation Criteria

Initial attempts to relate shear band initiation to the load-elongation curve slope were not precise. Therefore, shear band initiation was determined on a macroscopic level by visual observations and on a microscopic level by using a polariscope for observations. The method used to obtain microscopic shear band initiation was more reliable, but could only be used on the transparent materials. The less reliable method of visual observation had to be used on the opaque materials.

The macroscopic initiation of shear bands was determined by visual observation upon unloading. A

crossed field polariscope with white light was used for determining the microscopic level of shear band initiation. The specimen was loaded and then unloaded to see if residual strain existed. If one isochromatic line was visible along the maximum shear strain axis, the shear band was considered initiated. If a fringe remained for more than thirty seconds it was considered residual strain. Microscopic band initiation is indicated in the specimens of Figure 2.

3. Test Temperature

Varying temperatures were obtained by putting the specimens in an environment at the temperature desired for four hours and then quickly testing them at room temperature. Specimen tests were usually completed within two minutes after exposure to room temperature. The nominal temperatures are listed with their corresponding mixtures.

Dry ice and isopropyl alcohol	-75°C
Salt and snow	-21°C
Isopropyl alcohol and water	-15°C
Ice water	0-2°C
Oven	above 23.5°C

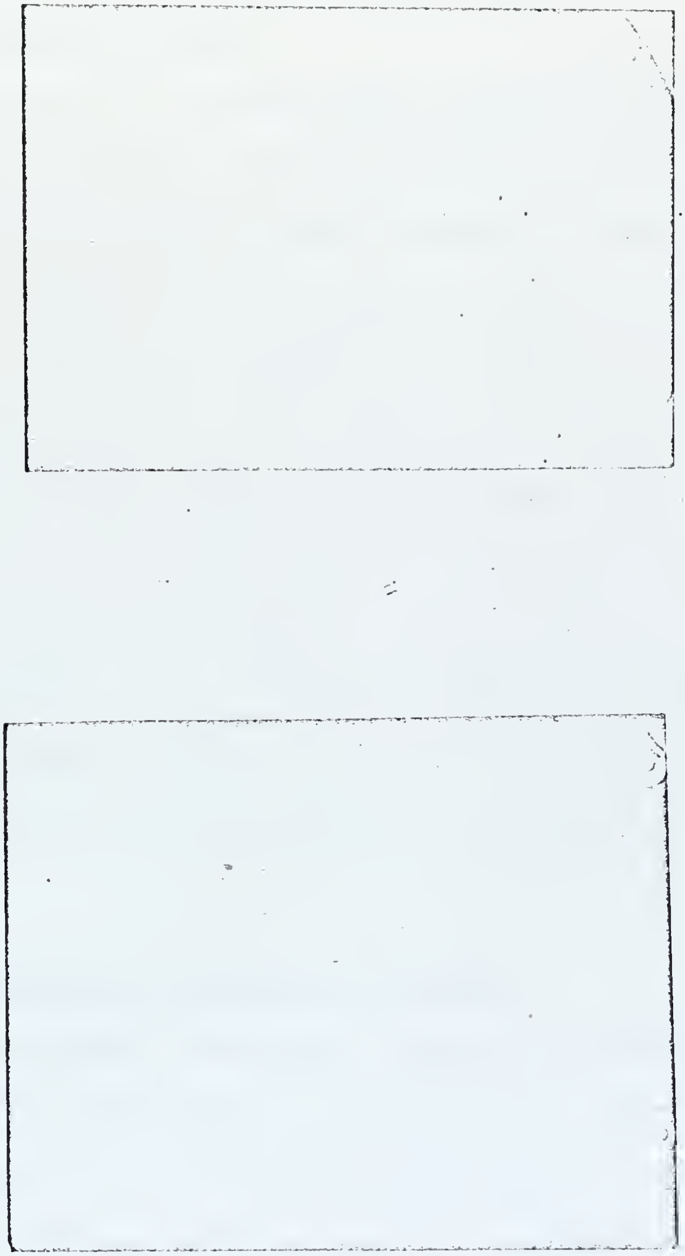


FIGURE 2. MICROSCOPIC BAND INITIATION.
ONE RESIDUAL FRINGE ON THE MAXIMUM SHEAR AXIS.

III. EXPERIMENTAL RESULTS

A. Deformation Band Initiation Stress

1. Nominal Stress

The nominal stresses were obtained by dividing the load from the Instron Testing Machine by the minimum cross sectional area of the specimen. The nominal stresses required for deformation band initiation in the materials tested are tabulated in Tables I-V of Appendix B. The maximum nominal stress (σ_N) is listed with the nominal macroscopic (σ_M) and/or the microscopic (σ_m) initiation stress. The H or L immediately following a tabulated value indicates the nominal stress is high or low due to a known reason, i. e. specimen poorly machined, specimem cracked during testing, specimen was not loaded to maximum or the band initiation criteria was exceeded during loading.

2. Effects of Residual Stresses

Photoelastic techniques indicated residual stresses existed after machining. Consequently, most specimens were annealed at 100°C for thirty minutes before testing. A comparison of the various nominal stresses in annealed and unannealed specimens milled from the same cast plate is shown in Table VI. No significant effect is apparent. In the low temperature cured epoxy (E 16xx

series) the maximum nominal stress (σ_N) indicates less stress required in the annealed case, but both maximum stress averages are based on only two specimens for each case. The microscopic initiation stress average of this series is of the same magnitude with or without the residual stresses.

3. Strain Rate Effect

The variation in the band initiation stress for the various normal strain rates is listed in Table VII and shown in Figure 3. The normal strain rate was obtained by dividing the crosshead speed by the gage length of the specimen (0.6 inches). The variation in normal strain rate was obtained by using crosshead speeds of .005, .05 and .5 in./min. The band initiation stress (σ_B) was obtained by multiplying the nominal microscopic stress (σ_m) by the appropriate stress concentration factor (SCF).

There appears to be no significant change in the EPON 828 between the low and medium strain rates. However, the rubber modified epoxy indicates a greater strain rate dependancy than the unmodified epoxy. The initiation stresses generally increase as the strain rate increases.

4. Variation with Test Temperature

The band initiation stress (σ_B) increases as temperature decreases. Figure 4 indicates the relation for

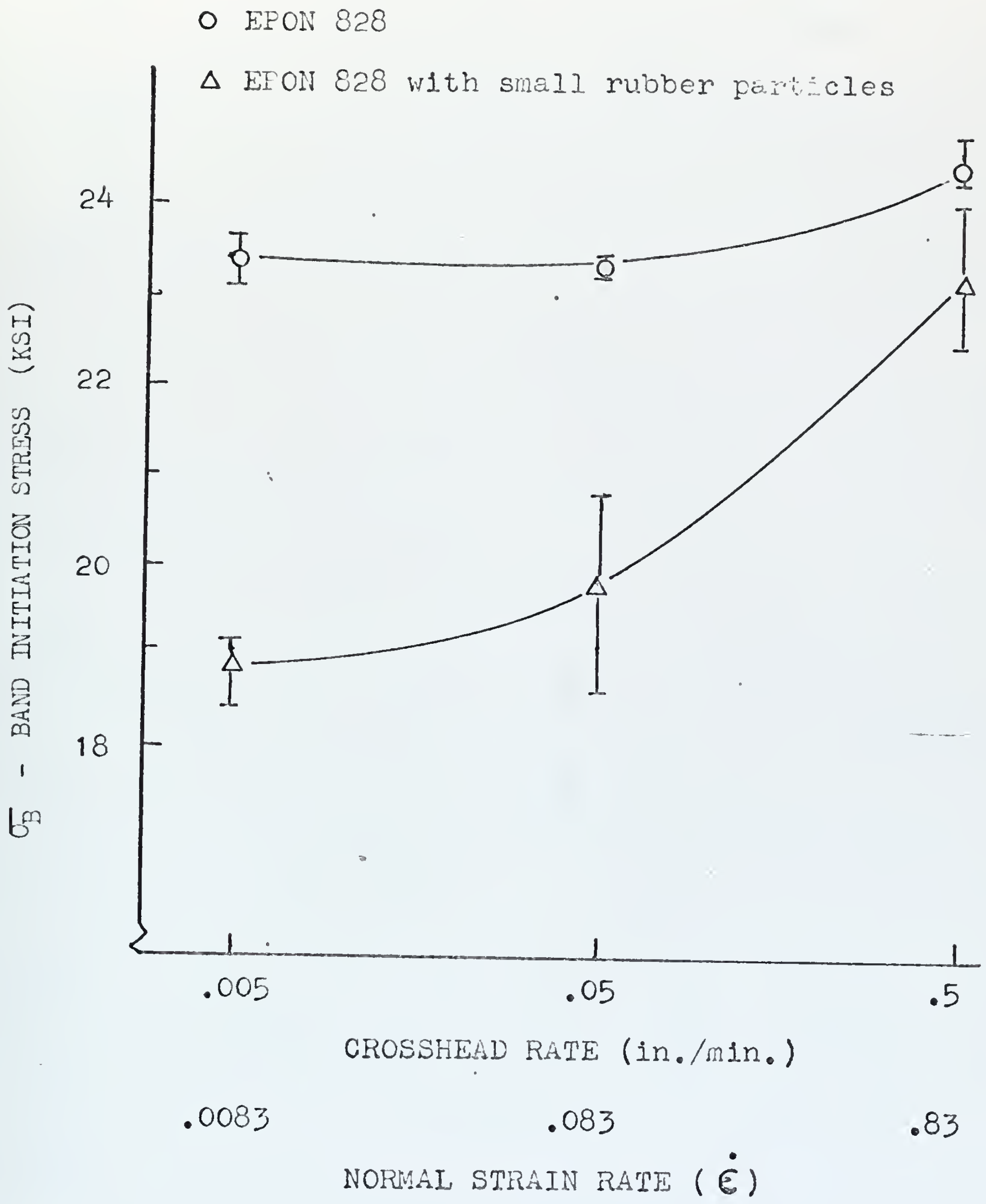


FIGURE 3. VARIATION OF INITIATION STRESS WITH STRAIN RATE.

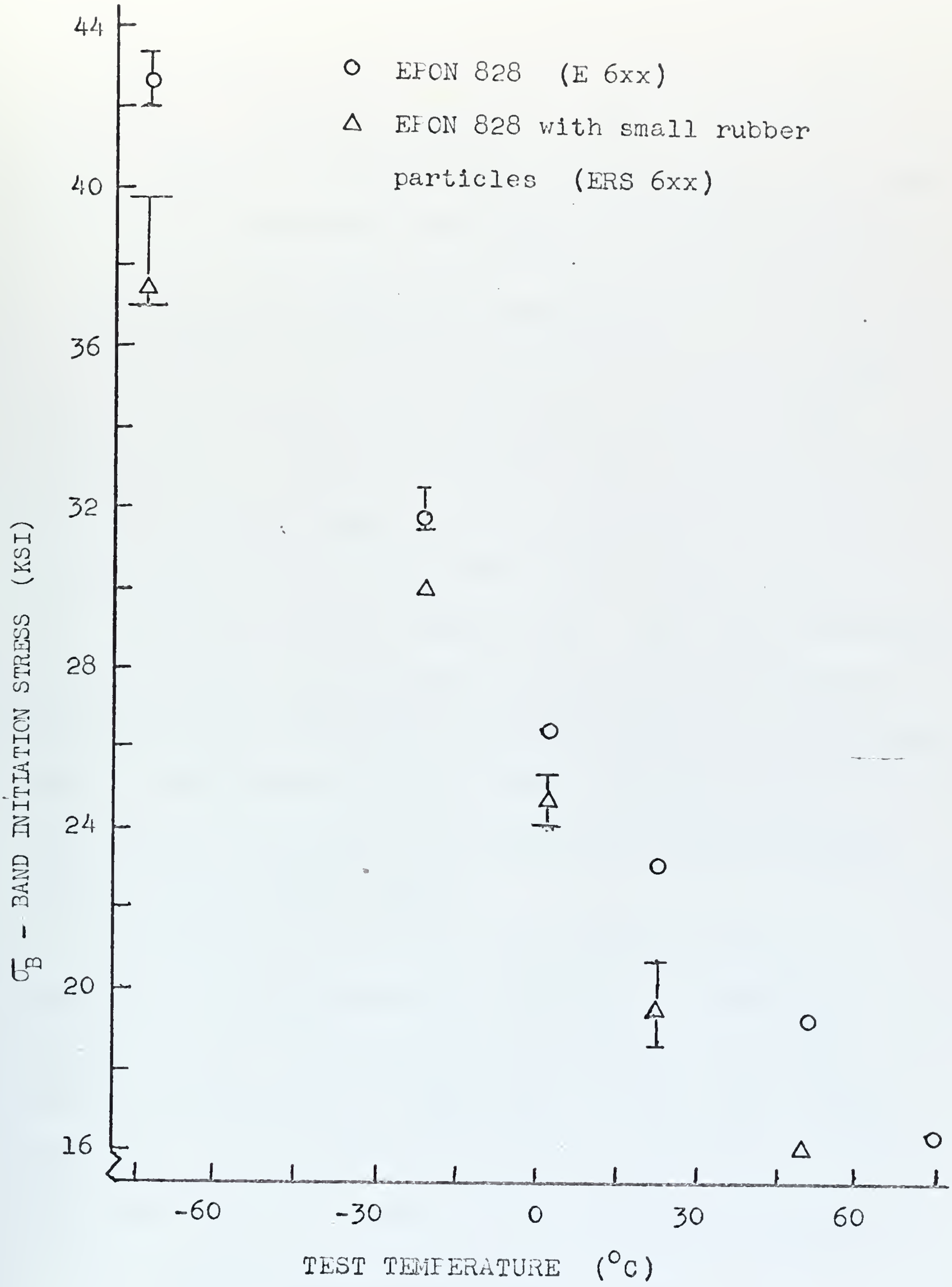


FIGURE 4. DEPENDENCE OF INITIATION STRESS ON TEST TEMPERATURE.

both EPON 828 and EPON 828 modified with small rubber particles. The band initiation stress in the modified epoxy appears to increase at a faster rate than the EPON 828 as the temperature decreases.

5. Variation with Cure Temperature

The band initiation stress in the rubber modified EPON 828 was normalized to EPON 828 for both curing temperatures. Figure 5 indicates that the bands in the EPON 828 with the small rubber particles initiate at 85 and 82% of those in the EPON 828 for the high and low temperature cures, respectively. The low temperature cured EPON 828 with the small particles was translucent while the high temperature cured EPON 828 was transparent. For the EPON 828 with large rubber particles, the macroscopic initiation stress (σ_M) was almost constant in the few specimens tested.

A difference of 3.3 ksi was observed between macroscopic and microscopic initiation in EPON 828. Using a 3.3 ksi difference, a microscopic initiation stress was obtained for EPON 828 with the large rubber particles. This estimated value for microscopic initiation stress (σ_m) was used for the comparison in Figure 5.

6. Stress Concentration Factor (SCF)

Specimen geometry is very critical in the area of

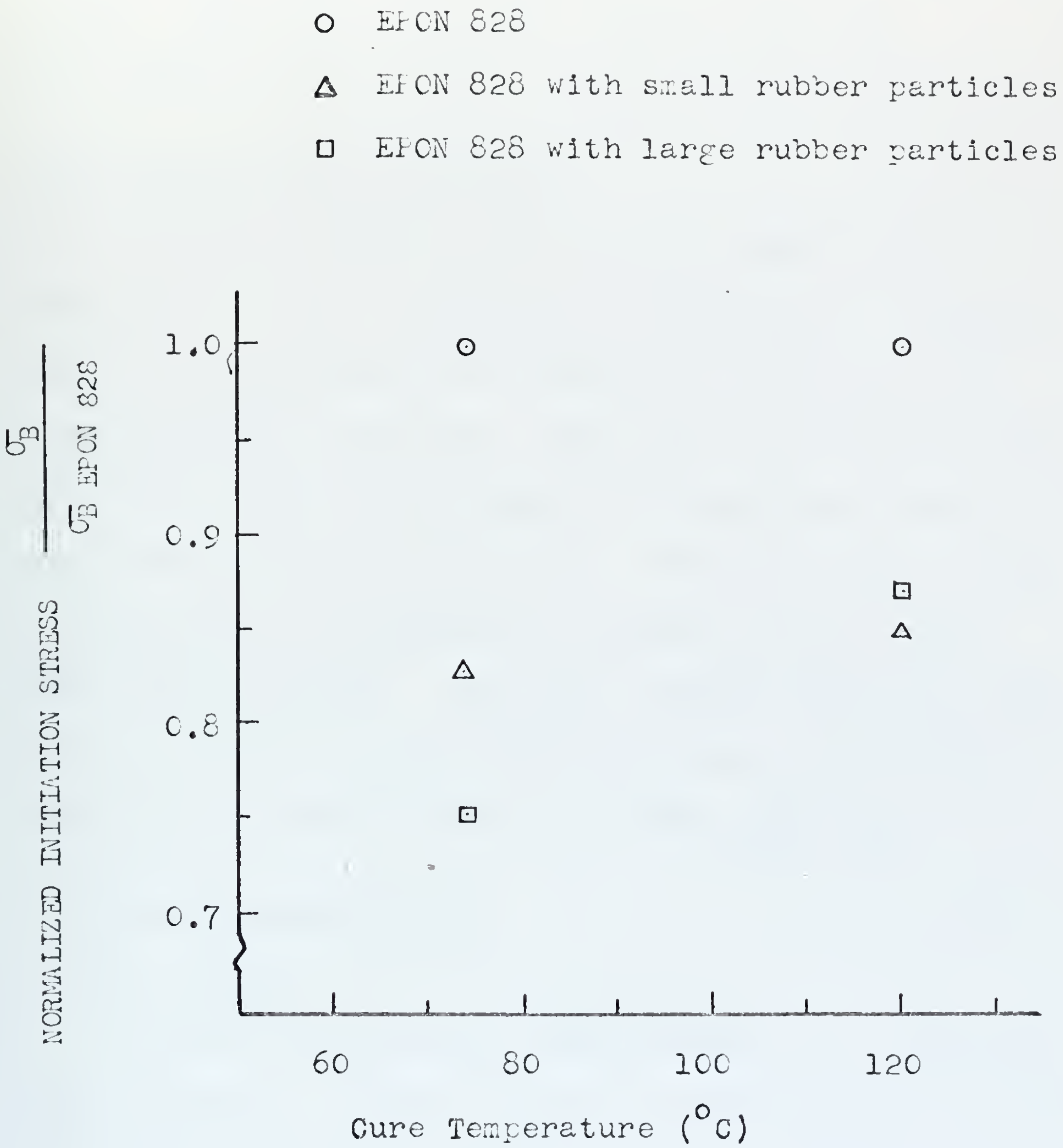


FIGURE 5. VARIATION OF NORMALIZED INITIATION STRESS WITH CURE TEMPERATURE.

a stress concentration. To examine the accuracy of the band initiation stress, the test results of single notched specimens were compared to those of holed specimens. The band initiation stresses were 30.0 - 31.5 ksi for a SCF of 3.3 and 23.2 - 23.4 ksi for a SCF of 2.35.

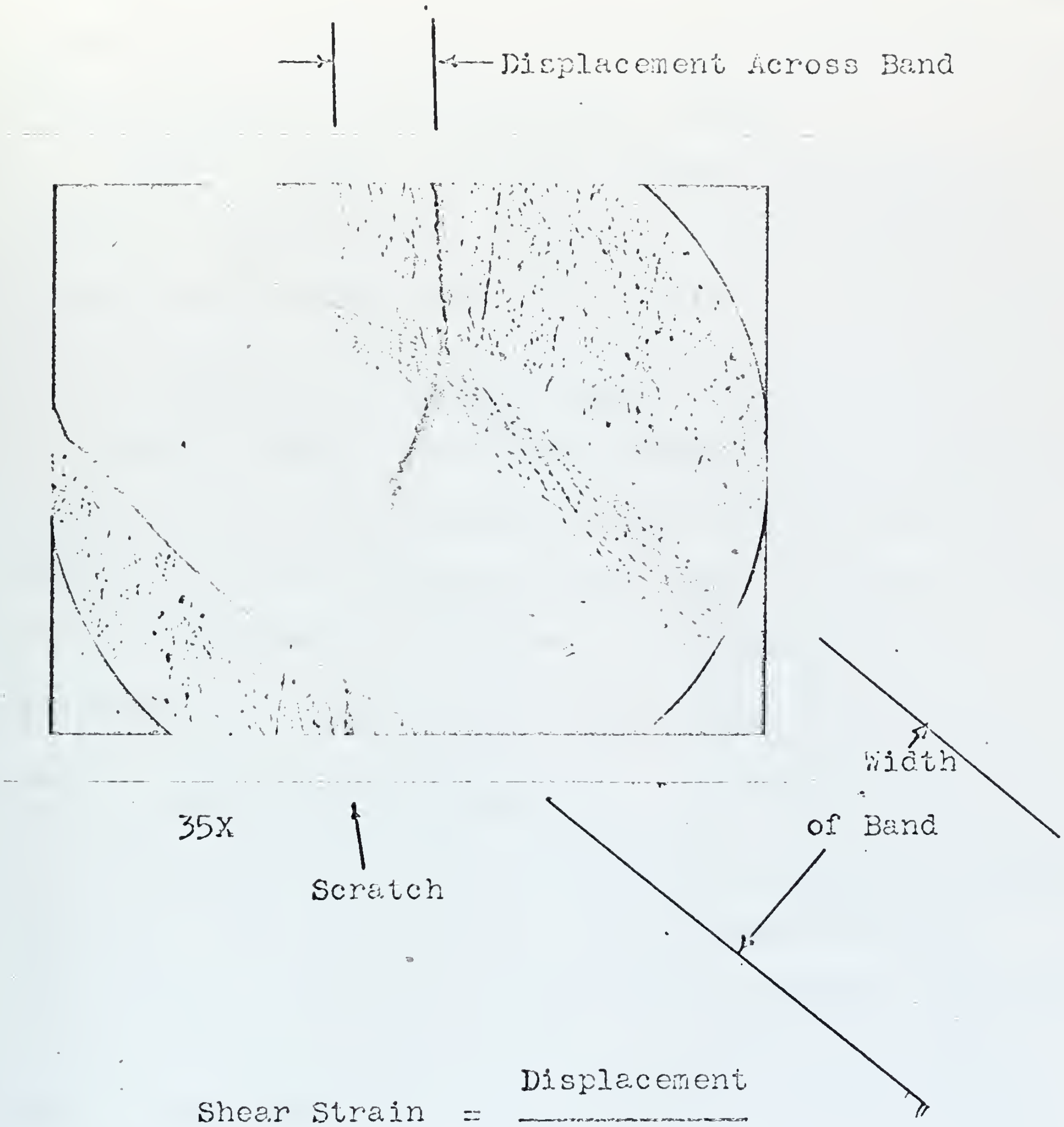
B. Strength after Annealing

Several specimens were tested, annealed, and retested. A few were annealed and retested a second time. All specimens were annealed at 100°C for 70 minutes before retesting. The results are tabulated in Table X. Most of the nominal stresses were reduced as the number of tests increased. There were some exceptions where the strength was greater on the second test than the first. The most notable groups were the high temperature cured EPON 828 (E 6xx) and EPON 828 modified with small rubber particles (ERS 6xx).

C. Band Characteristics

1. Strain

Strains in the bands were measured by a technique from Whitney[6]. Figure 6 shows the measurement of strain in an EPON 828 center holed specimen. Actually, this strain measurement is of the yield zone. Strains of 60% were observed in the notched specimen, but strains in bands initiated from a circular hole were generally less



$$\text{Shear Strain} = \frac{\text{Displacement}}{\text{Band Width}}$$

FIGURE 6. SHEAR STRAIN IN AN EPON 828 DEFORMATION BAND.

with an approximate maximum of 30%. The band strain is dependent upon the time and amount of loading. Specimens loaded for a longer time or to a higher load showed greater band propagation and higher band strain.

Figure 7 shows a notched specimen which was unloaded at maximum load. Figures 8 and 9 show the residual strains under polarized light.

2. Angle of Deformation Band

Several shear bands were observed under an optical microscope and the propagation angle varied from 37-47 degrees from the principal stress axis. Figures 10 and 11 are micrographs showing some typical angles of propagation.

3. Variation with Material

The yield zone was more diffuse in epoxy than polystyrene. Observations from a polarizing microscope indicate the yield zone in EPON 828 is several bands in a band packet as noted by Argon, et al.[12] The yield zone in ERLA 4617 appeared less diffuse than in epoxy. The low temperature cured EPON 828 and the unmodified ERLA 4617 appeared more brittle. The initiation stresses were larger and both cracked vertically as shown in Figure 12. Table XI shows a comparison of the band initiation stresses.

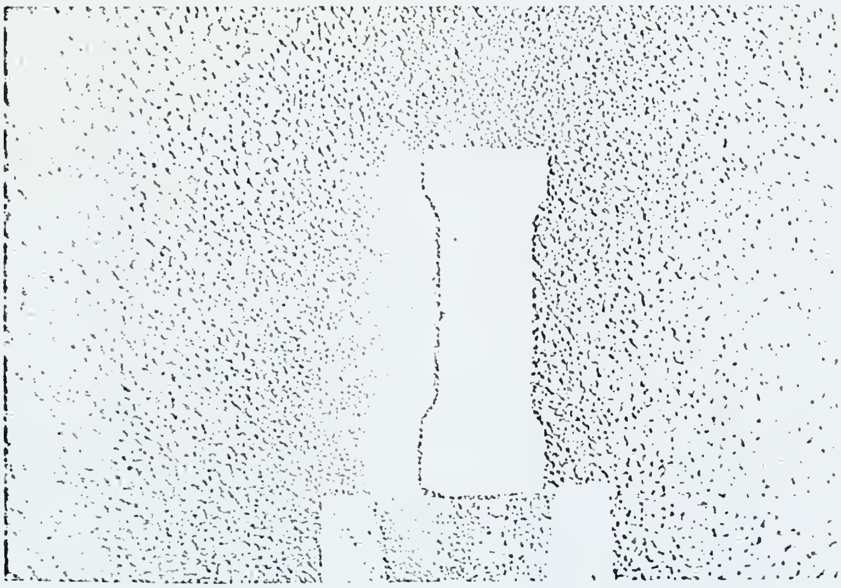


FIGURE 7. DEFORMATION BAND IN SINGLE NOTCHED SPECIMEN.

FIGURE 8. DEFORMATION BAND IN NOTCHED SPECIMEN VIEWED WITH POLARIZED LIGHT.

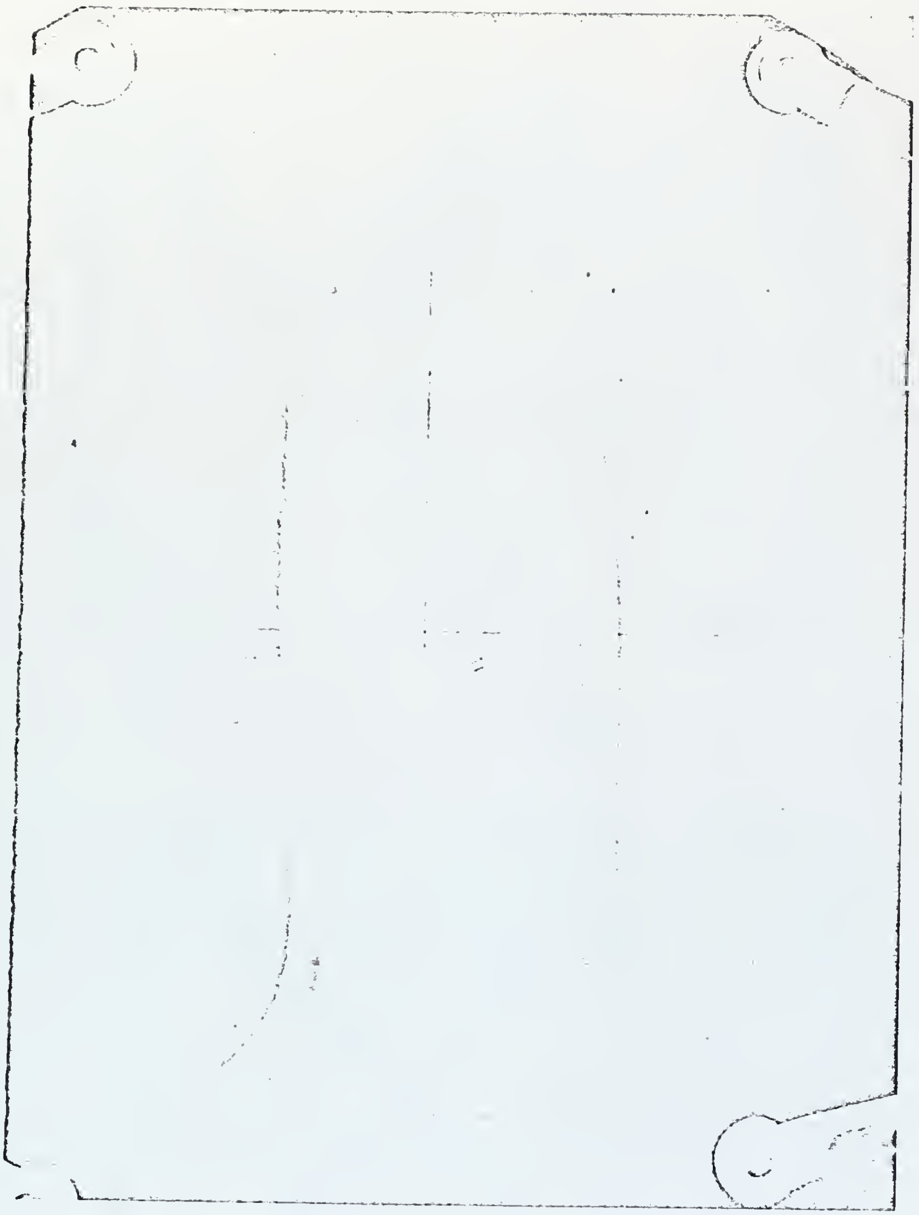
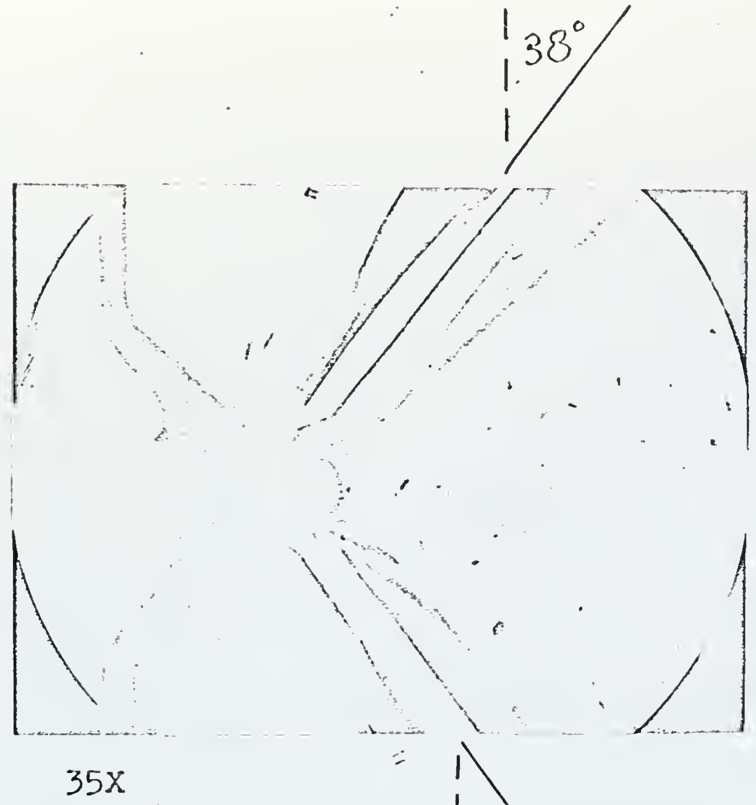


FIGURE 9. DEFORMATION BAND IN A HOLED SPECIMEN VIEWED WITH POLARIZED LIGHT.



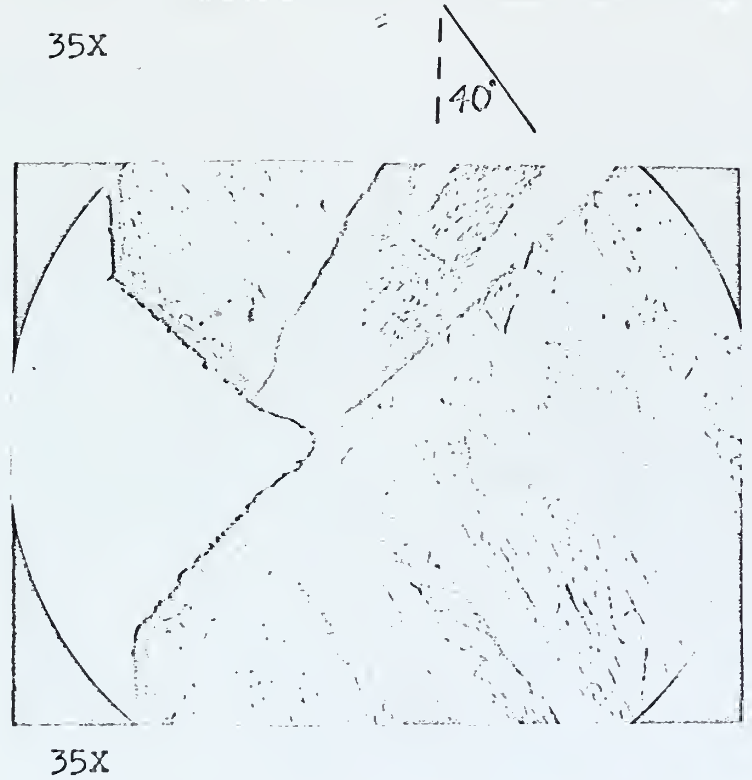


FIGURE 10. DEFORMATION BAND ANGLE IN A NOTCHED SPECIMEN.

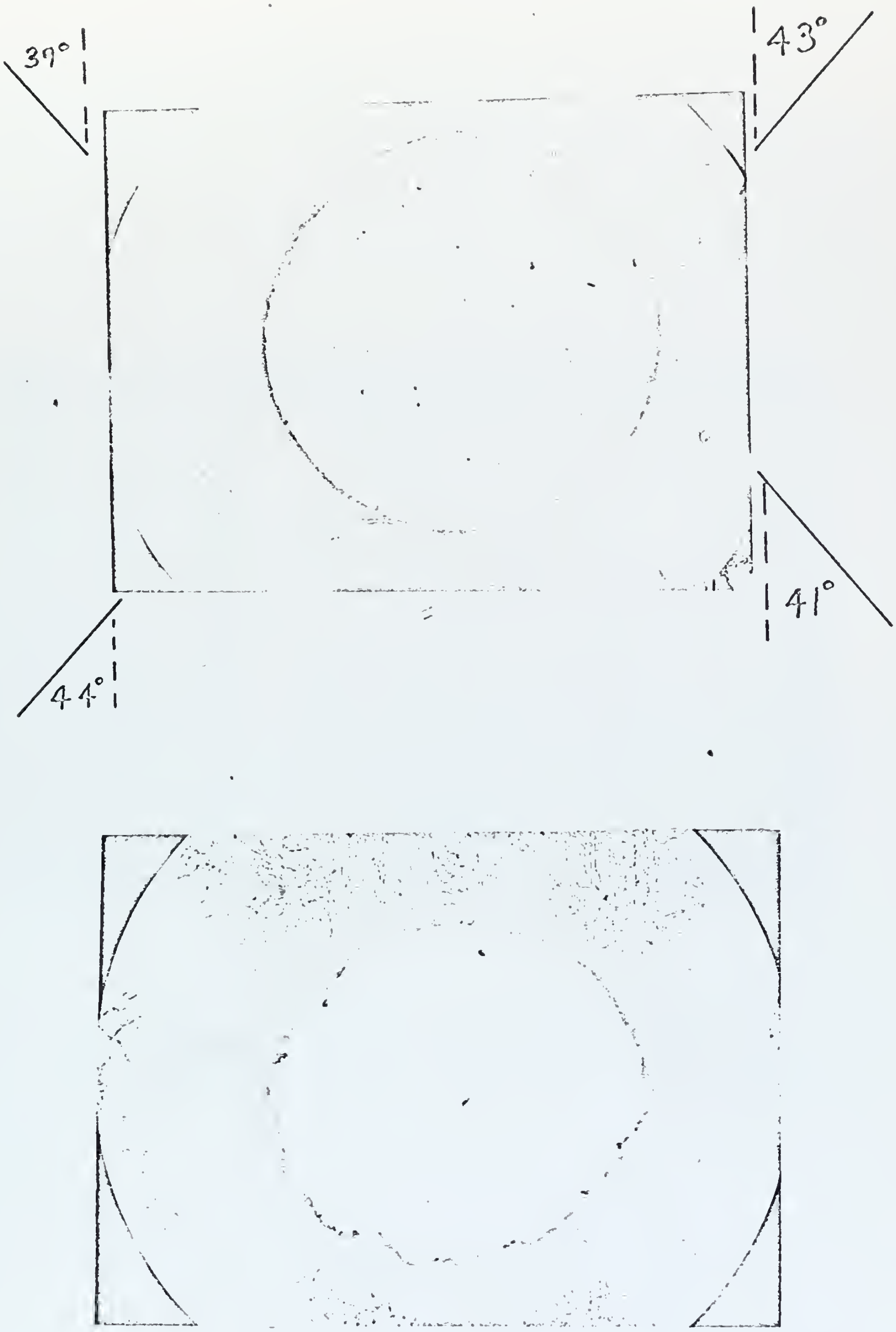


FIGURE 11. DEFORMATION BAND ANGLE IN A HOLED SPECIMEN (35X).

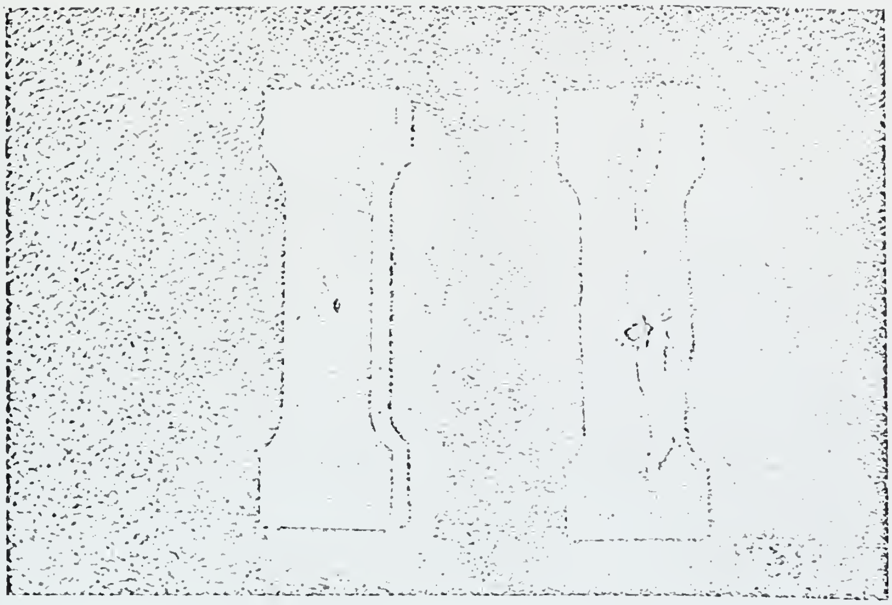


FIGURE 12. VERTICAL CRACKS IN BRITTLE SPECIMENS.

D. Fracture Surface Work

The fracture energy (γ) was calculated for the various cures and modifications of EPON 828 by a method to be documented by Schmidt.[13] The results are listed in Table XII.

IV. DISCUSSION AND CONCLUSIONS

A. Variation of Band Initiation Stress

1. Effects of Residual Stresses

The polariscope indicated a maximum residual strain equivalent to two isochromatic lines after machining. This indicates the residual compressive stress varied from zero to almost 200 psi. However, the results in Table VI indicate a majority of the specimens required a higher initiation stress with the residual stresses present. Therefore, one must conclude either the differences are within the experimental error or the annealing changes the properties of the material. The latter might be the case for the low temperature cured EPON 828 (E 16xx). The three unannealed specimens appeared to be more brittle, cracking close to maximum load. The vertical cracks are shown in Figure 12. However, the initiation stress was not altered significantly, so one must conclude the effects of residual stresses are minor and/or not detectable by this testing method.

2. Strain Rate and Test Temperature

Only EPON 828 and EPON 828 with 10% small rubber particles were tested at various strain rates and temperatures. The initiation stress shows the time-temper-

ature dependence as expected in a visco-elastic material. Figures 3 and 4 indicate the equivalent temperature for a 0.833 strain rate is 8 and 15°C for EPON 828 and EPON 828 with 10% small rubber particles, respectively. The lower strain rate is less sensitive showing an equivalent temperature of about 32°C for the modified EPON and no significant change from the .0833 strain rate for EPON 828. An exponential relation between initiation stress and strain rate would explain the greater sensitivity at high strain rates.

Figure 13 indicates the initiation stress to be linear with respect to the inverse of temperature. The discrepancy of the data at a -74°C is probably due to the temperature of the specimen increasing before testing was completed. The slight discrepancy at a -21°C is probably due to the increase in strain rate. The crosshead rate was increased to .2 in./min. at the two lower temperatures, -21 and -74°C, to decrease the exposure time at room temperature prior to test completion.

The initial attempt to identify the stress for shear band initiation to an exponential type relation is shown in Figure 14. One might conclude two processes are occurring with one dominating above 10°C and the other dominating below a -10°C. The variation is the

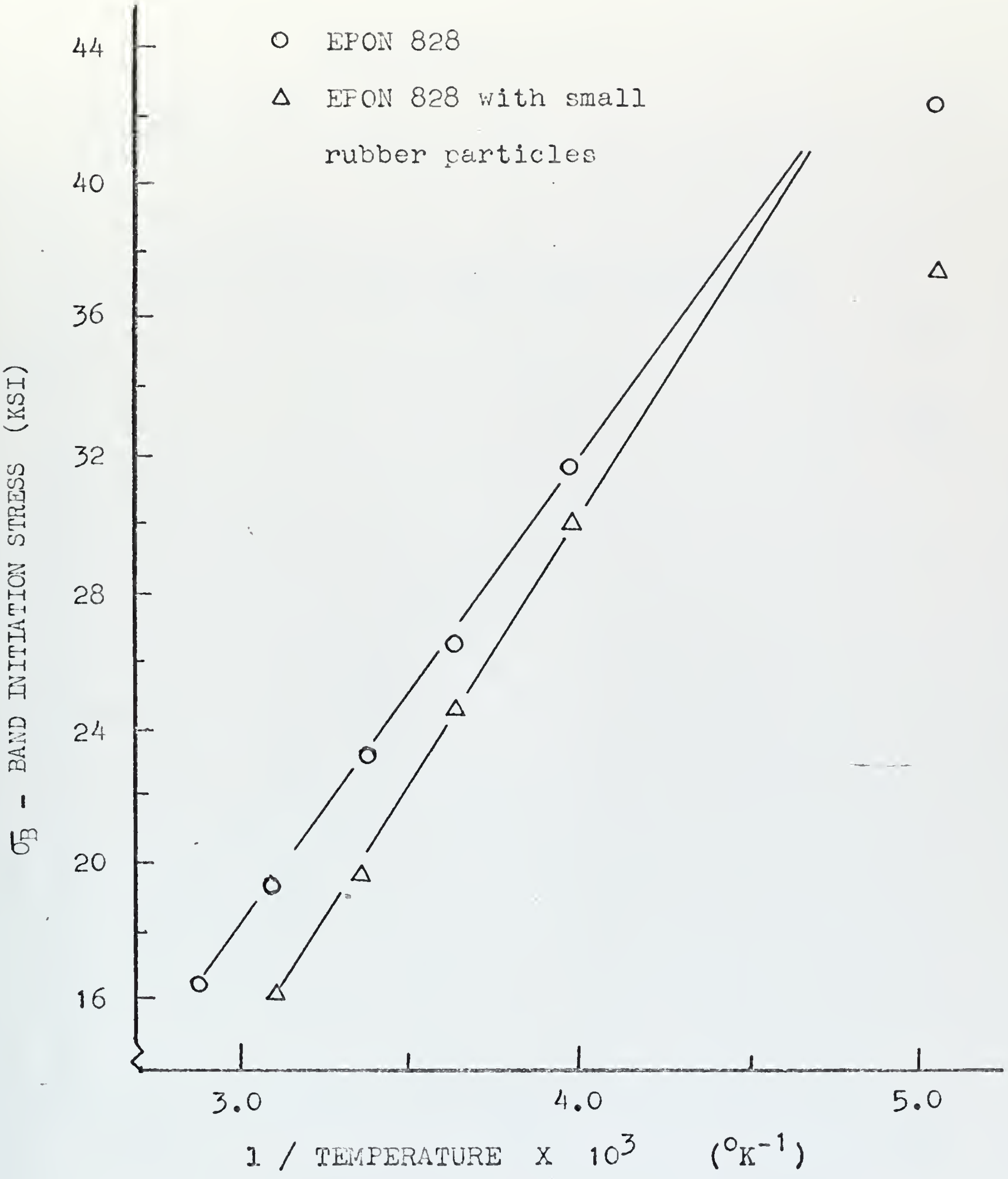


FIGURE 13. VARIATION OF INITIATION STRESS WITH THE INVERSE OF TEMPERATURE.

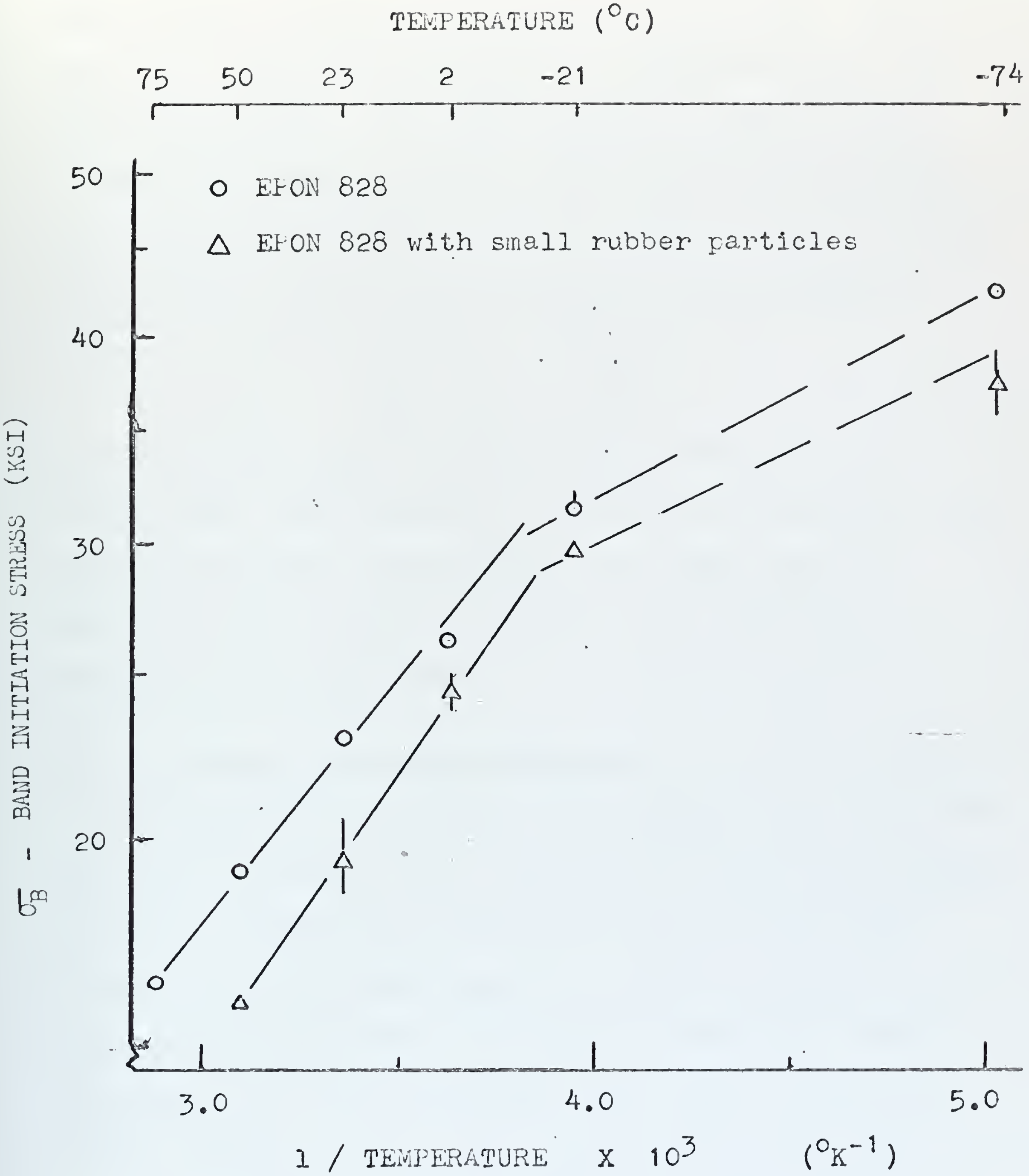


FIGURE 14. VARIATION OF INITIATION STRESS WITH TEMPERATURE (LOG PLOT).

same in both the modified and unmodified epoxy. Therefore, the controlling processes or mechanisms must be due to the matrix. It could be due to immobilization of molecular chain segments. Although further testing may substantiate this conclusion, one must conclude from the present data that shear band initiation stress follows a relation similar to equation (1)

$$\sigma_B = \sigma_o + m\ (1/T) \qquad (1)$$

where m is the slope and σ_o is the intercept of the stress axis. The values for the slope and intercept are probably dependent upon material and such that the band initiation stress is equal to the theoretical strength at absolute zero.

3. Curing Temperature Effects

Experiments by Sultan and McGarry[1] have indicated that cure temperature has little or no effect on particle size for a CBTN with a molecular weight of 5800 when cured with 4 pph Curing Agent D. However, the low temperature cured EPON 828 modified with small rubber particles was less transparent which might indicate a slight increase in the size of the rubber particles.

The reduced curing temperature might allow a higher degree of polymerization which probably increases the molecular weight and strength of the EPON 828.

The increase of band initiation stress in low temperature cured EPON 828 and EPON 828 modified with small rubber particles is shown in Table IX. However, there is no apparent explanation for the cure temperature insensitivity of the initiation stress in EPON 828 modified with the large rubber particles. It is noted that the material was opaque and band initiation was determined on the macroscopic level.

4. Stress Concentration Factor

There is 700-800 psi difference in band initiation stress between the holed and notched specimens. This is probably due to the holed specimens having an actual stress concentration factor greater than 2.35. A microscopic comparison of the machined surfaces indicates the hole to have greater surface imperfections than the notch. Consequently, the actual band initiation stresses for the holed specimens are probably somewhat greater than reported here.

Figures 10 and 11 indicate neither the notch nor the hole to be completely smooth. Microscopic stress concentrations cause the bands to initiate at points away from the theoretical maximum stress concentration such as the bottom of the notch.

B. Strength after Annealing and Retesting

Annealed specimens appeared unchanged from the original untested condition. Although some specimens showed an increase in strength, most indicated reduced strength upon retesting. All specimens showed reduced strength upon the third test. The average reduction in strength between two successive tests is listed in Table XIII and the results are inconclusive. However, it is the opinion of the author that the density in the area of band propagation is decreased due to "minute" voids formed when local chains or crosslinks break. The voids are probably due to the few per cent of molecular chains or crosslinks that break and do not reform during stress relaxation. Once a break occurs, the chain relaxes and the local free volume, in the area of the break, increases. As adjacent chains relax (break and reform), the local material undergoes flow. Most of the localized flow is due to the breaking of secondary bonds (Van der Waals) which is recoverable upon annealing. However, the molecular chains that do not reform or reform in a different location upon stress relaxation and annealing are responsible for the strength deterioration.

C. Band Characteristics

The angle and manner of band propagation should really not be considered unusual. Nadai[14] reported that in the case of flat silicon steel specimens the parallel slip lines developed at certain equal intervals. He also reported the flow lines did not become thicker after they appeared on the sides of the flat bar, but new finer lines appeared between the slip lines already formed. Nadai[15] also predicted that Luders' lines must be expected in other metals if the material has a well-defined yield point and a slight stress concentration helping to start or develop these single plastic layers.

Nadai[16] reasoned that there must be a contraction of 1-2 per cent in the flow line because the bounding part of the test piece does not change its dimensions. He also reported that the angle of slip lines with axis of the specimen was usually a little greater (47°) in the case of tension and a little less then 45 degrees in the case of compression.

Whitney[6] and Argon et al.[12] have reported similar observations in thermoplastic polymers. Similar characteristics have been observed in thermoset polymers. Therefore, it seems reasonable to conclude that these flow lines could be observed in most materials. Although the necessary conditions to form flow lines are

not understood, a well-defined yield point and a means of stress concentration appear to be sufficient.

D. Stress Criteria for Band Initiation

1. Mohrs' Theory of Strength

> "The condition under which solid materials begin to deform permanently or a stressed body breaks according to Otto Mohr can be formulated in a general manner. A material may fail either through plastic slip or by fracture when either the shearing stress (τ) in the planes of slip has increased to a certain value which in general will depend also on the normal stress (σ) acting across the same planes or when the largest tensile normal stress has reached a limiting value dependent upon the material."[17]

According to Mohr, the largest principal circles represent the states of stress at the limits of plasticity or at the limits of fracture and have an enveloping curve which is represented in Figure 15 by the two tangential lines. Argon, et al.[12] used a special case of the Mohr Theory of Strength to justify the band angles in polystyrene of 38 degrees in tension and 52 degrees in compression tests.

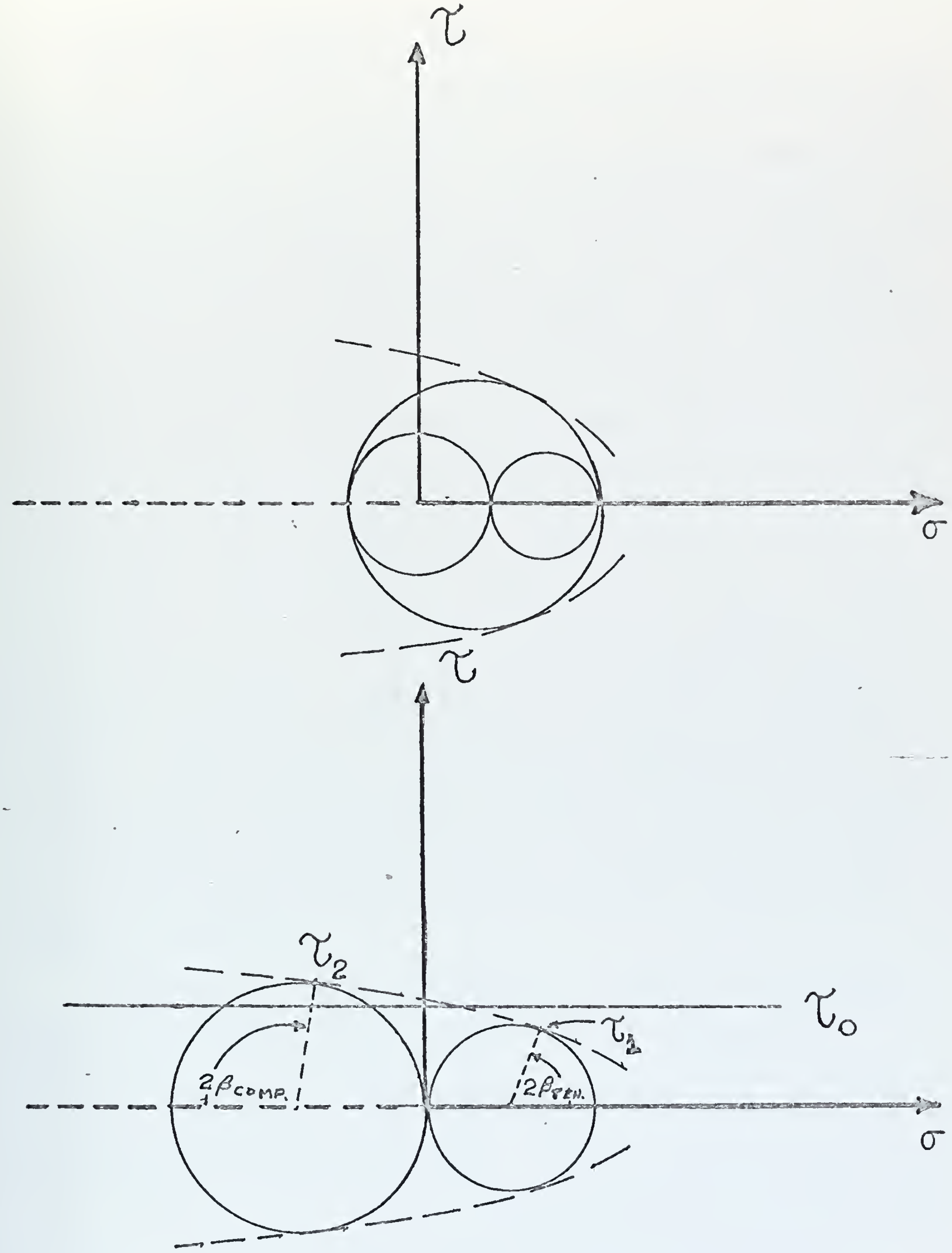


FIGURE 15. MOHR ENVELOPE.

2. Shear Stress Criteria

The Mohr Theory of Strength is probably applicable to the thermoset polymers. The Mohr Theory does predict the compressive yield stress to exceed the tensile yield stress which is commonly known. No bands were formed in tension in the unmodified EPON 828, but the angle of the bands in compression varied from 37-47 degrees. Figures 10 and 11 indicate most bands initiated at an angle less than 45 degrees. Some angles increased after significant band propagation. The change in angle is due to the local changes in the stress field. Maximum shear contours for a hole in Hookean solids indicate the orientation of the shear plane is different for each point on the contour. A figure by Sternstein et al[18] indicates the maximum shear plane for uniaxial tension to be at an angle much less than 45° adjacent to the edge of the hole.

Assuming the Mohr Envelope to define the maximum shear stress and knowing bands do not initiate in tension, one might select a shear stress (τ_o) as the criteria for band initiation. Figure 15 indicates that $\tau_2 > \tau_o > \tau_1$ and the bands should not initiate in tension. This idea of a shear stress criteria was suggested by Sultan and McGarry[1].

3. Effects of Rubber Particles

a. Variation of Initiation Stress with Test Temperature

The rubber particles should cause some stress concentration factor due to the bonding boundary. However, the particles are still rubbery and probably do not attain the theoretical maximum stress concentration. The maximum theoretical stress concentration for a sphere in an infinite body in uniaxial tension is two and is located at the equator. However, if the particles are bonded to the matrix they should exert a radial tensile stress on the matrix due to their higher thermal coefficients of expansion. This would cause the epoxy interface to be under tangential compression or a compressive hoop stress at the equator. Beck et al[19] calculated a compressive stress of 363 psi for impact polystyrene at a temperature 50°C below the forming temperature.

Figure 16 shows Mohrs' Circle for the typical values of applied initiation stress at 23.5°C for the EPON 828 and epoxy modified with small rubber particles. As the temperature decreases the compressive stress in modified epoxy will increase and a larger applied stress will be required to initiate shear bands. Since the matrix properties vary with test temperature, conclusions can only be made by comparing the initiation stresses in the modified and unmodified epoxy. There-

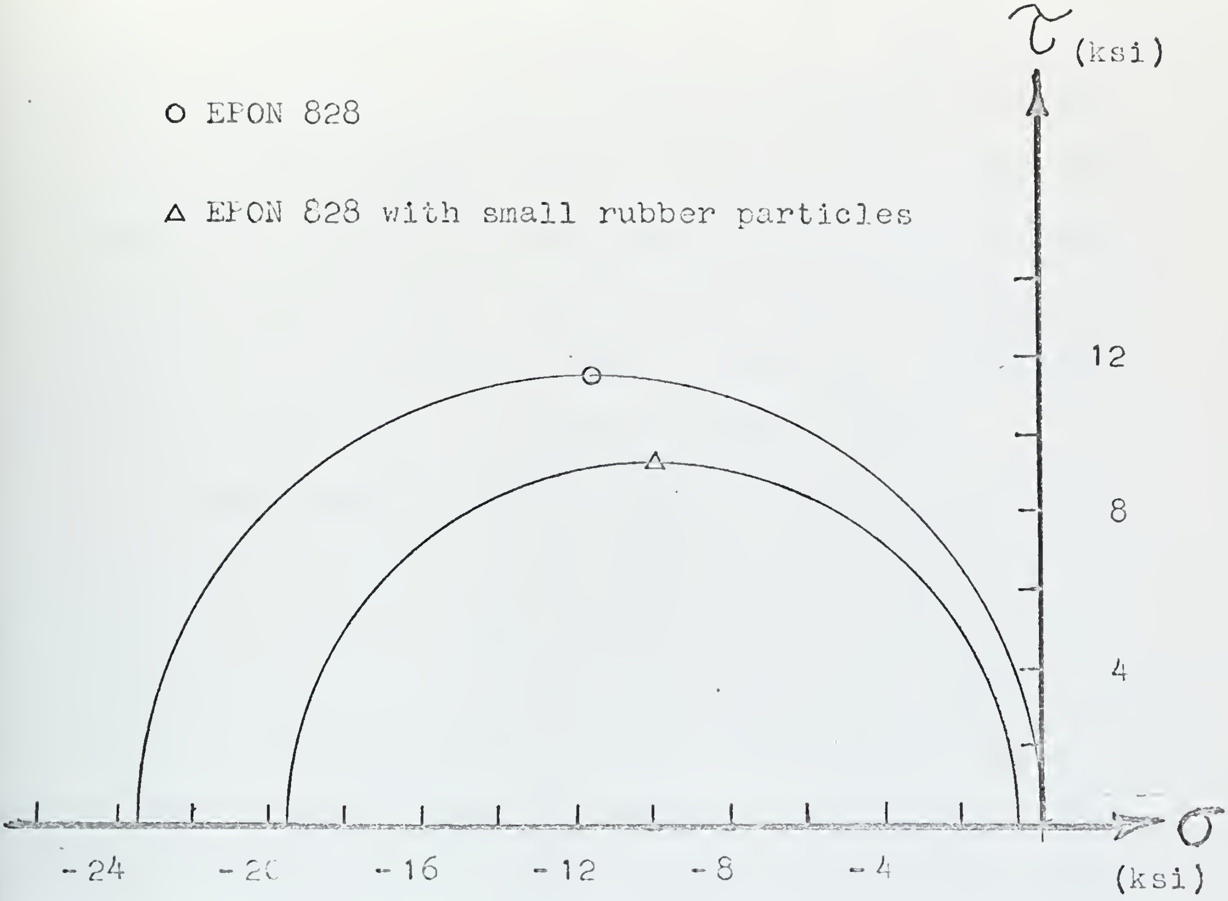


FIGURE 16. MOHRS' CIRCLE FOR STANDARD SPECIMEN SERIES TESTED AT ROOM TEMPERATURE.

fore, the initiation stress of the modified epoxy should approach that of the unmodified. Figure 13 indicates this is the case if the data point at a -74°C is ignored. Also, the ratio of the modified to unmodified initiation stresses should approach unity as the temperature decreases. Figure 17 indicates this may be the case on a qualitative basis. The data at -74°C is probably in error, but no apparent reason is known for the sudden drop in the ratio of the two specimen series.

Quantitative studies based on the difference of initiation stresses were inconclusive. Calculations based on a constant SCF for the rubber particles and including or not including the compressive test failed to obtain the same shear stress criteria as observed in the matrix. The calculations, including the compressive stress, were at best estimates since this stress level is only a few per cent of the applied stress and the experimental data has around 5 per cent scatter.

b. Variation of Initiation Stress with Strain Rate

Figures 3 and 4 show the correlation between strain rate and temperature which is as expected from the time temperature superposition principle. However, by comparing the modified to the unmodified epoxy the change in initiation stress due to time and temperature should

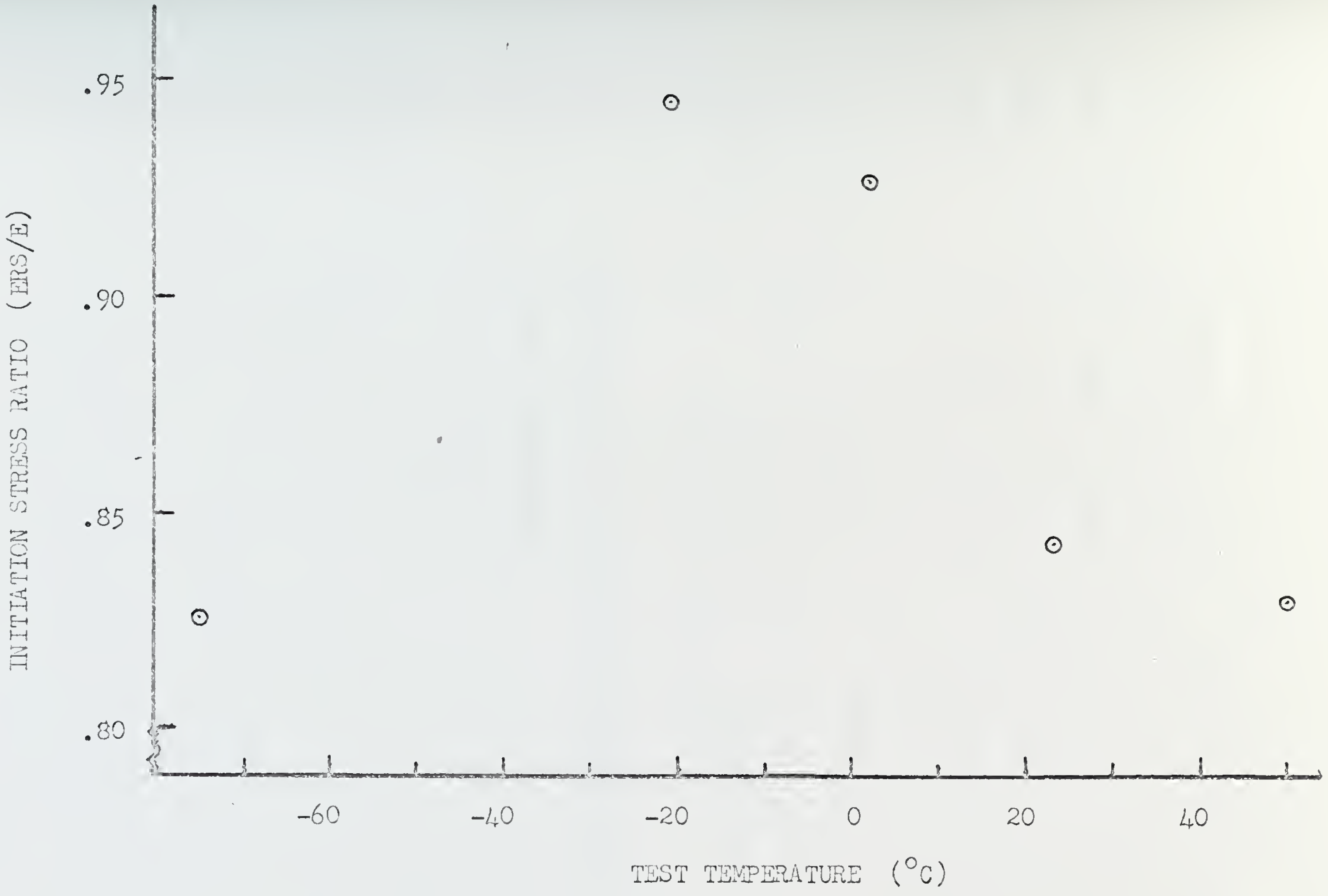


FIGURE 17. VARIATION OF MODIFIED TO UNMODIFIED INITIATION STRESS RATIO WITH TEST TEMPERATURE.

be normalized and only the difference of initiation stresses should change the slope of the curve. This was done in Figures 17 and 18. These figures indicate the difference in initiation stress to be more strain rate sensitive than temperature sensitive. This data again qualitatively confirms the idea of a compressive stress by the rubber particles, but the quantitative difference in initiation stress connot be related to the compressive stress due to the rubber particles. Also, the increase in strain rate sensitivity is not predicted if the only change is a linear change in the compressive stress with temperature.

c. Variation of Initiation Stress with Cure Temperature

If the cure temperature is decreased, the compressive stress of the rubber particles on the matrix should decrease because the difference between the forming temperature and test temperature is reduced. Consequently, the initiation stress should increase as the cure temperature is decreased. Once again changes are noted in the matrix and only the difference of initiation stresses or their ratio is an appropriate comparison. The ratio should approach unity as the cure temperature approaches test temperature.

Table IX indicates an increase of 1 ksi in the

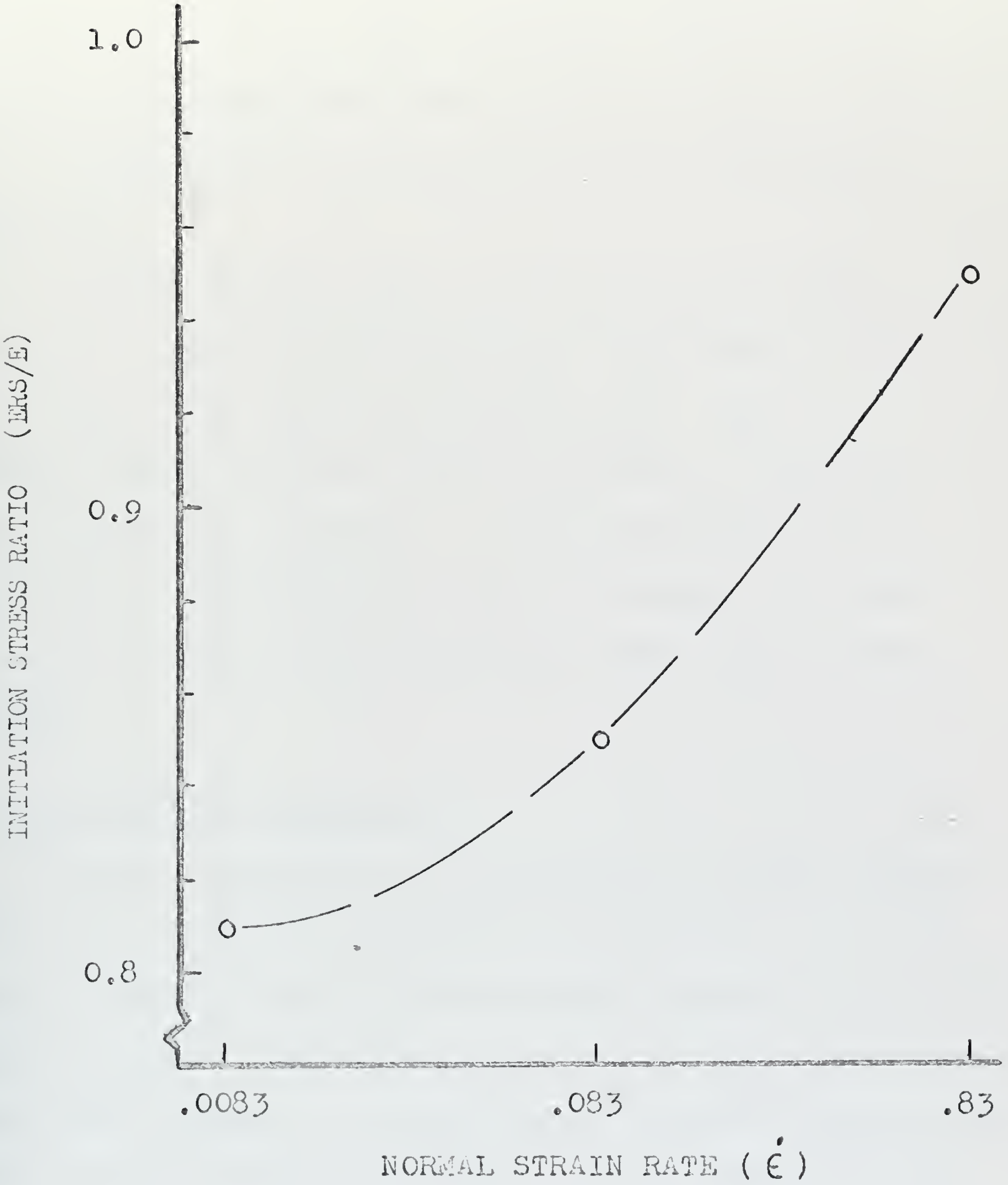


FIGURE 18. VARIATION OF MODIFIED TO UNMODIFIED INITIATION STRESS RATIO WITH STRAIN RATE.

epoxy with small particles by changing the cure temperature from 120 to 74°C. However, the initiation stress of the EPON 828 increased by 1.6 ksi and the ratio tends away from unity as the cure temperature decreases.

Earlier in this report it was noted that the molecular weight of the epoxy and the rubber particle size may change with cure temperature. There are several other variables whose influence is unknown. The temperature influence on the curing agent may be important. Consequently, any conclusions from tests using cure temperature variations might not be justifiable.

E. Deformation Mechanism

Various mechanisms for yielding in glassy polymers have been proposed and partially justified. The shear stress criteria for band initiation appears to be in the same category. The criteria for shear flow should depend upon shear stress. A shear stress criteria when coupled with the Mohr Theory of Strength appear sufficient to explain shear band initiation in EPON 828. Some qualitative comparisons between rubber modified and unmodified epoxy tend to support the shear stress criteria for band initiation in rubber modified epoxy. However, quantitative studies could not support this criteria when

the rubber paricles were assumed only to exert a compressive stress on the matrix. Furthermore, qualitative and quantitative studies indicate that the rubber particles do not act simply as a constant stress concentration mechanism.

Yielding or band initiation in thermoset polymers is known to be a function of time, temperature, strain rate and probably pressure. The band initiation stress in EPON 828 seems to have a limited analogy to the failure of mild steel proposed by Nadai[20]. He stated that after the resistance of the reinforcing frame around the ferrite grains has been diminished the latter are severely deformed by shear and their lattice structure is further damaged within the regions of the thin layers in which the plastic distortion is localized. An analogy might apply to the interlocked, coiled molecules of polymers. Upon the separation of these interlocks (may be covalent bonds) a few chains are probably broken and then the molecular chains may elongate by orientating.

The molecular activity is pressure, temperature, strain and strain rate dependent. It must be this activity which controls the interlocking forces. The molecular activity is easily changed by varying molecular weight, cross linking and type of polymerization.

The exact influence of rubber particles upon local molecular activity is not known.

If we assume the interlocking force to be covalent bonds, the dissociation energies are of the order of 50-200 kcals/mole. The energy to break the C-C aliphatic bond is 60-70 kcals/mole. Values for the activation energy of shear bands is believed to be in the 20-40 kcals/mole range. Consequently, either a weaker primary bond exists in the chain or the dissociation energy is somehow decreased when shear bands initiate.

Another unlikely possibility is that shear band initiation is controlled by the intermolecular cohesion forces which are due to a combination of secondary forces: Van der Waals, Dipole, Induction and Dispersion Forces. This would cause band initiation to be temperature, time, strain rate and pressure dependent. However, it does not account for the loss of strength upon annealing and retesting.

It is possible that rubber particles do somehow form weaker bonds and the 10% rubber added could easily account for the 0-5% loss of strength. However, this mechanism cannot account for the loss of strength in unmodified EPON 828 unless minute amounts of impurities (maybe water) also cause the formation of weak bonds.

The author's opinion is that shear bands initiate

due to a reduction in the dissociation energy of the primary bond. Roetling[21] showed that the dependence of tensile yield stress upon temperature and rate of strain could be described in terms of the Ree-Eyring rate process theory. A good fit between experiments and theory could be obtained only if two processes were considered. He found the activation energy of the segmental process to be 98 and 32 kcals/mole with the higher activation energy process appearing to predominate in the glassy state and the lower activation energy process at higher temperatures.

Andrews[22] indicates that stress alone is capable of depressing the glass transition. Thus, stress level, coupled with the rule of mixtures for determining the glass transition temperature (T_g) copolymers, explains most of the experimental results. First, the mixing of rubber particles lowers T_g at the rubber particle matrix interface where shear bands probably initiate. The stored elastic energy will then propagate it similar to the propagation of a crack. If the propagation is arrested, the elastic energy will again be stored and a new shear band will initiate when the critical stress level is reached. The amount of stress required to obtain T_g probably varies with the inverse of temperature.

If the ratio of the elastomer to the epoxy in the interface is assumed constant, the T_g should be lowest in

the EPON 828 with the large rubber particles. This is due to the increased amount of butadiene in the large elastomer which lowers its glass transition temperature.

In the low temperature cured epoxy, the increased molecular weight may increase T_g and thereby the initiation stress. The rubber particles decrease T_g, but not to the same level as before. This is indicated by an increase in the stress level to form bands in modified and unmodified specimens with a low temperature cure.

The strain rate, pressure, temperature and time dependence of shear band initiation is also greatly influenced by the intermolecular cohesion forces. Thus, the level of molecular activity and the dissociation energy of primary bonds are believed to be the controlling mechanism for shear band initiation.

V. SUGGESTIONS FOR FUTURE WORK

A. Effects of Rubber Particles

Further study into the mechanism of band initiation and the influence of the rubber particles is required. Further investigations are required to determine the stress concentration factor caused by the rubber particles and its variation with stress, time and temperature. An initial value can be obtained by performing a compressive test at the cure temperature.

Further study on the process of adding rubber particles and their micromolecular influence on the dissociation energy of the primary and secondary bonds. This study should include large rubber particles.

B. Activation Energy and Volume

The activation energy should be obtained for modified and unmodified epoxy to insure the same mechanism is responsible for band initiation. The activation volume should also be obtained to indicate the unit volume of flow, i.e. chain segment length. The activation energy and volume are probably stress and temperature dependent.

C. Shear Stress Criteria

It appears that there exists some critical shear stress at which bands will initiate. It is dependent upon many parameters and the quantitative variation

must be obtained from theory and experiments.

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APPENDIX A

DEFINITION OF SYMBOLS

SCF	Stress Concentration Factor
ϵ	Normal Strain
$\dot{\epsilon}$	Normal Strain Rate
γ	Fracture Surface Work
σ_B	Band Initiation Stress (Local Stress at Microscopic Shear Band Initiation) $\sigma_B = SCF \times \sigma_m$
σ_m	Nominal Stress at Microscopic Shear Band Initiation
σ_M	Nominal Stress at Macroscopic Shear Band Initiation
σ_N	Maximum Nominal Stress

APPENDIX B

TABULATED RESULTS

TABLE I

NOMINAL STRESS VALUES FOR BAKELITE, ERLA 4617

Specimen		σ_N (ksi)	σ_M (ksi)	σ_m (ksi)	Test Temp (°C)	Crosshead Rate (in/min)	Notes
B	001	28.30			*	*	1,2
	002	23.90					1,2
	600	25.20					1,2
	601	28.70					1,2
BRX	600	25.56	19.46H				1,2
	601	25.42	19.55H				1,2
	602	21.00	20.00H				1,2
	603	20.75	19.75				

* A blank in these columns indicates the tests were conducted at the standard temperature of 23.5°C and a crosshead rate of .05 in./min.

Note 1 This specimen was tested using the rolling bearing base to insure parallel faces.

Note 2 The residual stresses from machining were not annealed from this specimen.

TABLE II

NOMINAL STRESS VALUES FOR EPON 828

Specimen	σ_N	σ_M	σ_m	Test Temp	Crosshead Rate	Notes
	(ksi)	(ksi)	(ksi)	(^oC)	(in/min)	
E 043	12.40	11.14	9.54	*	*	2,4
044	12.33	11.58L	9.12			2,4
046						2,3,4
045	12.37	11.68	9.12			2,4
047	11.68	11.49	9.42			2,4
048	12.35	11.63	9.08			2,4
501	12.65					1,2,4
502	12.42					1,2,4
601	14.25					1,2,4
602		14.05				1,2,4
603	15.40	14.90				1,2,4
604	13.65	13.30				1,2,4
605	16.05	15.80				1,2,4
606		15.30				1,2,4
607	15.40	15.20				1,2,4
608	15.88	15.36				1,2,4
609	15.81	15.32				1,2,4
610	16.60	16.05H				2,4
611	15.10	14.85				4
612	15.07	14.82	12.30H			4

Specimen	$\sigma_{\overrightarrow{N}}$	$\sigma_{\overrightarrow{M}}$	$\sigma_{\overrightarrow{m}}$	Test Temp	Crosshead Rate	Notes
	(ksi)	(ksi)	(ksi)	(°C)	(in/min)	
E 613	15.20	14.10		*	*	4
614		14.00				4
615	15.40L	15.37				4
616	17.10			1		4
617	17.10			1		4
618	16.30L	16.15		1		4
619	16.15			1		4
620	16.30	16.34		1		4
621	17.26			-16		4
622	15.80		13.55	-16		4
623	16.30L	16.20	14.00	-16		4
624	16.15L	16.10		-16		4
625	16.10	16.00		-16		4
626	14.60		11.20H	50		4
627	14.78	13.90		50		4
628	15.35	14.50	11.00H	50		4
629	14.95	13.55	10.20	50		4
630	14.85	13.85	10.50H	50		4
631	15.20	14.00	10.35	50		4
632				100		3
633				100		3
634				100		3
635				100		3
636	10.80			75		

Specimen	σ_N (ksi)	σ_M (ksi)	σ_m (ksi)	Test Temp (°C)	Crosshead Rate (in/min)	Notes
E 637	12.13H		7.08	75	*	
638	11.70		7.01	75		
639			7.07	75		
640			9.03H	50		
641	12.40		8.27	50		
642	12.35		8.25	50		
643	12.32		8.30	50		
644	13.80		11.33	2		
645	13.80		11.26	2		
646	13.00		9.86			
647	13.10		9.87			
648	12.67		9.86			
649	13.15		9.95			
650	13.20		10.60H			
651	13.60		10.90H			
652						3
653						3
654						3
655	14.09		11.31	2		
656	13.55		11.27	2		
657	13.80		11.19	2		
658	13.78		11.34	2		
659			13.50	-21		

Specimen	σ_N	σ_M	σ_m	Test Temp	Crosshead Rate	Notes
	(ksi)	(ksi)	(ksi)	(^{o}C)	(in/min)	
E 660			13.86	-21	.2	
661			14.55H	-21	.2	
662			13.45	-21	.2	
663			13.47	-21	.2	
664			18.05	-74	.2	
665			17.88	-74	.2	
666			16.60L	-74	.2	
667			18.50	-74	.2	
668			15.50L	-74	.2	
669			18.13L	-74	.2	
670	12.34		10.32H		.005	
671	12.52		9.93		.005	
672	12.30		10.05		.005	
673	12.60H		9.97		.005	
674	12.03		9.85		.005	
675	14.13				.005	
676	13.40		12.05H		.5	
677	13.65		10.56		.5	
678	13.80		10.33		.5	
679	13.36		10.35		.5	
680	13.82		10.57		.5	
681	12.52		10.13L		.5	
682						

Specimen	σ_N	σ_M	σ_m	Test Temp	Crosshead Rate	Notes
	(ksi)	(ksi)	(ksi)	(^{o}C)	(in/min)	
E 683						3
801	13.08					1,2,4
802	12.10					1,2,4
803	13.02					1,2,4
804	12.50					1,2,4
805	12.75					1,2,4
806	13.00					1,2,4
807	12.48					1,2,4
1600			11.44			2
1601	15.50		11.35			2
1602	16.50		11.40			2
1603			11.40			
1604			11.49			
1605			11.48			
1606	14.85		11.60			
1607	15.20		11.35			
603-1	14.92	13.40	12.50H			4
604-1	15.00	14.60	11.30			4
605-1	15.82	15.07	12.05			4
606-1	15.20	15.00	11.50			4
607-1	15.85	15.50	13.20H			4
608-1	15.85	15.25L	12.16H			4
609-1	15.50	15.30	13.03H			4
610-1	15.40	15.40	13.75H			4

Specimen	σ_N	σ'_M	σ_m	Test Temp	Crosshead Rate	Notes
	(ksi)	(ksi)	(ksi)	(°C)	(in/min)	
E 611-1	13.70		11.10	*	*	4
612-1	13.50		10.96			4
613-1	14.05		11.05			4
614-1	14.00		11.05			4
646-1	13.20		10.18			
647-1	13.16		10.55			
648-1	13.10		10.32			
649-1	13.20		10.59			
650-1	13.40		10.40			
651-1	13.31					
1603-1	14.70		10.63			
1604-1	14.50		11.12			
1605-1	14.20		10.70			
1606-1	14.35		10.81			
1607-1	14.60		11.10			
610-2	13.50		10.96			4
611-2	13.47		10.68			4
612-2	13.30		10.71			4
613-2	13.53		10.65			4
614-2	13.35		10.70			4

*, Notes 1 & 2 See footnotes of Table I.

Note 3 Specimen was not tested.

Note 4 Milled from E xxx cast plate #1 vice #2.

TABLE III

NOMINAL STRESS VALUES FOR EPON 828 WITH 10% LARGE RUBBER PARTICLES

Specimen	σ_N	σ_M	σ_m	Test Temp	Crosshead Rate	Notes
ERL 001	10.53			*	*	1,2
002	10.00					1,2
003	9.68					1,2
004	10.70					1,2
005	10.88					1,2
006	10.96					1,2
601	13.35	12.07				2
602	13.39	11.72				2
603	13.52	11.15L				2
604	13.60	10.70L				
605	13.63	12.50L		0		
606		12.80		0		
607	14.10			0		
608	13.32	12.88		0		
1600	12.78	12.07				
1601	12.45	11.80				
1602	12.92	12.10				
1603		12.05				
1604	12.07	11.41				
1605	12.25					
1606	12.23	11.88				

Specimen	σ_N (ksi)	σ_M (ksi)	σ_m (ksi)	Test Temp (°C)	Crosshead Rate (in/min)	Notes
ERL 1607				*	*	3
1608						3
601-1	12.90					
602-1	12.95	12.20				
603-1	13.00	10.90L				
604-1	11.00	10.20				
605-1	10.85	10.67				
606-1	10.85					
607-1	10.85	10.15				
608-1	10.88	10.18				
1600-1	12.07	10.98				
1601-1	11.80	10.92				
1602-1	12.15	11.01				
1603-1	11.82	10.95				
1604-1	11.50	10.10				
1605-1	11.80	10.70				
1606-1	11.45	10.80				
601-2	11.50	10.30				
602-2	11.40	10.50				
603-2	11.40	10.66				

*, Notes 1 & 2 See footnotes of Table I

Note 3 Specimen was not tested.

TABLE IV

NOMINAL STRESS VALUES FOR EPON 828
WITH 10% SMALL RUBBER PARTICLES

Specimen		σ_N	σ_M	σ_m	Test Temp	Crosshead Rate	Notes
		(ksi)	(ksi)	(ksi)	(^{o}C)	(in/min)	
ERS	600	12.00		9.08H	*	*	
	601	12.20		8.52			
	602	12.02		7.93			
	603	12.02		7.94			
	604	12.30		8.40			
	605	12.10		8.56			
	606				100		3
	607				100		3
	608				75		
	609				75		
	610				75		
	611	6.92		3.34	75		
	612	11.10		6.92	50		
	613	11.05		6.86	50		
	614	11.10		6.86	50		
	615	11.03		6.85	50		
	616				100		3
	617				100		3
	618	13.10		10.32	2		
	619	13.12		10.72	2		

Specimen	σ_N	σ_M	σ_m	Test Temp	Crosshead Rate	Notes
	(ksi)	(ksi)	(ksi)	(°C)	(in/min)	
ERS 620	12.90		10.60	2		
621	12.60		10.42	2		
622	12.80		10.82	2		
623	12.78		10.42	2		
624			15.75L	-74	.2	
625			14.80L	-74	.2	
626			15.76	-74	.2	
627			16.90	-74	.2	
628			15.20	-74	.2	
629			16.12	-74	.2	
630			8.34			2
631	12.03		8.83			2
632	11.98		8.40			2
633			14.92H	-21	.2	
634			15.00H	-21	.2	
635			12.82	-21	.2	
636			12.70	-21	.2	
637			12.84	-21	.2	
638	10.30		8.17		.005	
639	10.77		8.12		.005	
640	10.34		8.12		.005	
641	10.56		8.14		.005	
642	10.15		7.85		.005	
643	10.57		7.84		.005	

Specimen	σ_N	σ_M	σ_m	Test Temp	Crosshead Rate	Notes
	(ksi)	(ksi)	(ksi)	($^{\circ}$C)	(in/min)	
ERS 644	11.88		9.57	*	.5	
645	12.40		10.10		.5	
646	12.10		10.25		.5	
647	11.90		9.78		.5	
648	12.02		10.38H		.5	
649	11.71		9.58		.5	
650						3
651						3
652						3
1601	12.42		9.08			
1602	12.53		9.35			
1603	12.32		9.86			
1604	11.65		9.23			
1605	12.60		9.48			
1606	12.50		9.36			
1607						3
1608						3
600-1	12.20		8.40			
601-1	11.96		8.40			
602-1	11.80		8.38			
603-1	11.70		8.64			
605-1	12.10		8.73			
630-1	11.65		8.70			

Specimen	σ_N	σ_M	σ_m	Test Temp	Crosshead Rate	Notes
	(ksi)	(ksi)	(ksi)	(°C)	(in/min)	
ERS 631-1	12.20		8.73	*	*	
632-1	11.75		8.87			

*, Notes 1 & 2 See footnotes of Table I.

Note 3 Specimen was not tested.

TABLE V

NOMINAL STRESS VALUES FOR POLYSTYRENE

Specimen	σ_N	σ_M	σ_m	Test Temp	Crosshead Rate	Notes
	(ksi)	(ksi)	(ksi)	(°C)	(in/min)	
P 002	13.90	12.10		*	*	1,2
003	15.00	12.00				1,2
005	14.70	13.20				1,2
006	13.77					1,2
007	13.96	11.18				1,2
008						1,2
009	15.81	12.13				1,2
501	14.65	11.50				1,2
502						3
503						3
002-1	15.10	11.90				
004-1	15.33	12.92				
005-1	14.55	12.01				
006-1	15.03	11.90				
002-2	13.50	10.34				
004-2	14.07	11.13				
005-2	14.20	11.50				
006-2	12.17					

*, Notes 1 & 2 — See footnotes os Table I.

Note 3 — Specimen was not tested.

TABLE VI

EFFECTS OF RESIDUAL STRESS

Nominal Stress	Specimen	Annealed (ksi)	Unannealed (ksi)
Maximum	E 6xx	15.2	15.4
	E 16xx	15.0	16.0
	ERS 6xx	12.2	12.0
Band Initiation			
Macroscopic	E 6xx	14.6	14.9
Microscopic	E 16xx	11.5	11.4

TABLE VII

STRAIN RATE EFFECT

Strain Rate	Ave. Band Initiation Stress		Ratio
	E 6xx (ksi)	ERS 6xx (ksi)	ERS/E
0.833	24.5	23.2	.95
0.0833	23.3	19.8	.85
0.00833	23.4	18.9	.81

TABLE VIII

DEPENDENCE OF INITIATION STRESS ON TEST TEMPERATURE

Test Temp. (°C)	Specimen	Initiation Stress (σ_B) (ksi)
75	E 637	16.6
75	638	16.5
75	639	16.6
50	641	19.4
50	642	19.4
50	643	19.5
23.5	646	23.2
23.5	647	23.2
23.5	648	23.2
23.5	649	23.4
2	644	26.6
2	645	26.5
2	655	26.6
2	656	26.4
2	657	26.3
2	658	26.6
-21	659	31.7
-21	660	32.6
-21	661	34.2 High
-21	662	31.6
-21	663	31.6

Test Temp. (°C)	Specimen		Initiation Stress (σ_B) (ksi)
-74	E	664	42.4
-74		665	42.0
-74		666	39.0 Low
-74		667	43.4
-74		669	42.6
50	ERS	612	16.2
50		613	16.1
50		614	16.1
50		615	16.1
23.5		601	20.0
23.5		602	18.6
23.5		603	18.6
23.5		604	19.7
23.5		605	20.1
23.5		630	19.6
23.5		631	20.8
23.5		632	19.7
2		618	24.2
2		619	25.2
2		620	24.9
2		621	24.5
2		622	25.4
2		623	24.5
-21		635	30.1

Test Temp. (°C)	Specimen	Initiation Stress (σ_B) (ksi)
-21	ERS 636	29.8
-21	637	30.2
-74	624	37.0 Low
-74	626	37.0
-74	627	39.7
-74	628	35.7
-74	629	37.9

TABLE IX

VARIATION OF INITIATION STRESS WITH CURE TEMPERATURE

Cure Temp. (°C)	Material	Nominal Initiation Stress (ksi)
74	EPON 828	11.45
74	EPON 828 with large particles	8.65
74	EPON 828 with small particles	9.40
120	EPON 828	9.87
120	EPON 828 with large particles	8.60
120	EPON 828 with small particles	8.40

TABLE X

NOMINAL INITIATION STRESS VARIATION WITH NUMBER OF TESTS

Specimen	Number of test		
	1 (ksi)	2 (ksi)	3 (ksi)
E 603	14.90	13.40	
604	13.30	14.60	
605	15.80	15.07	
606	15.30	15.00	
607	15.20*	15.50	
609	15.32	15.30	
611		11.10	10.68
612		10.96	10.71
613		11.05	10.65
614		11.05	10.70
646	9.86*	10.18	
647	9.87*	10.55	
648	9.86*	10.32	
649	9.95*	10.59	
1603	11.40	10.63	
1604	11.49	11.12	
1605	11.48	10.70	
1606	11.60	10.81	
1607	11.35	11.10	
ERL 601	12.07		10.30

Specimen		Number of test		
		1	2	3
		(ksi)	(ksi)	(ksi)
ERL	602	11.72*	12.20	10.50
	603	11.15 Low	10.90 Low	10.66
	604	10.70 Low	10.20	
	1600	12.07	10.98	
	1601	11.80	10.92	
	1602	12.10	11.01	
	1603	12.05	10.95	
	1604	11.41	10.10	
	1605		10.70	
	1606	11.88	10.80	
ERS	601	8.52	8.40	
	602	7.93*	8.38	
	603	7.94*	8.64	
	605	8.56*	8.73	
	630	8.34*	8.70	
	631	8.83	8.73	
	632	8.40*	8.87	
P	002	12.10	11.90	10.34
	004	13.20	12.92	11.13
	005	13.20	12.01	11.50

* Indicates specimens which had a greater strength during a retest after annealing.

TABLE XI

BAND INITIATION STRESS FOR VARIOUS MATERIALS

Material	Band Initiation Stress (σ_B) (ksi)
B	56 - 63 #
BRX	34 - 36 #
E 6xx	23.3
E 16xx	26.8
ERL 6xx	20.2 #
ERL 16xx	20.3 #
ERS 6xx	20 - 21
ERS 16xx	22.1
P	23 - 28 #

# Indicates stress is an estimate based on only a few tests or on macroscopic initiation stress.

TABLE XII

FRACTURE SURFACE WORK

Material	Cure Temp. (°C)	Fracture work (γ) (ergs/cm^2) x 10^{-5}	
EPON 828	120	1.0 - 1.8	
	74	.5 - .7	
EPON 828 with small particles	120	1.8 - 3.0	
	74	3.4 - 4.0	
EPON 828 with large particles	120	15.0	
	74	2.1 - 3.3	
ERLA 4617	--	0.4	#
ERLA 4617 with CBTNX	--	1.4 - 2.0	#

# Data to be documented by Laible[9].

TABLE XIII

REDUCTION IN INITIATION STRESS UPON RETESTING

The average difference between nominal initiation stresses for two consecutive tests is listed for several series of specimens. The number in parenthesis after the difference is the number of specimens used to obtain the average. In two series there were a significant number of specimens which showed increased strength upon retesting. Consequently, there are two differences for those series which contained specimens going against the trend. The contrary difference is denoted by an asterick and is also negative.

Specimen Series	Differences (psi)	
	1 & 2	2 & 3
E 6xx	630 (4)	330 (4)
	-620 (6)*	
E 16xx	530 (5)	
ERL 6xx	500 (1)	500 (2)
ERL 16xx	1090 (6)	
ERS 6xx	110 (2)	
	-690 (5)*	
P 0xx	520 (3)	610 (3)

TABLE XIV

VARIATION OF MODIFIED TO UNMODIFIED INITIATION STRESS RATIO WITH TEMPERATURE

The following tabulation is the average initiation stress for the two series of specimens indicated and the number in parenthesis is the number of specimens from which the average stress was obtained.

Test Temp.	Ave. Initiation Stress		Ratio
	E 6xx	ERS 6xx	ERS/E
(°C)	(ksi)	(ksi)	
75	16.55 (3)		
50	19.43 (3)	16.13 (4)	.831
23.5	23.25 (4)	19.64 (8)	.844
2	26.50 (6)	24.79 (6)	.934
-21	31.80 (4)	30.03 (3)	.945
-74	42.60 (4)	37.56 (4)	.835

APPENDIX C

SPECIMEN PREPARATION PROCESS

The specimen preparation process consisted of the following procedures: mold preparation, mixing, curing, and machining. The mold preparation procedure consisted of cleaning two 12" by 12" glass plates and then coating them with two coats of mold release, FreKote 33[#], allowing at least ten minutes between coats for drying. A ½ inch thick rubber gasket was cut from a neoprene rubber sheet. The plates were then secured to the gasket with binder clamps. The mold and the oven were preheated to 120°C and were then ready for the liquid resin.

The mixing procedure for EPON 828 was to weigh the EPON 828 (400 grams) in a glass beaker, and then add 5 pph by weight (20 grams) of Curing Agent D. The mixture was heated in an oil bath at 175°F and slowly stirred until it was homogeneous. It was then poured into the preheated mold.

The mixing procedure for rubber modified EPON 828 was complicated due to the necessity of removing the air bubbles. The EPON 828 was weighed as indicated above and then 10 pph by weight (40 grams) of elastomer was added. The mixture was heated in an oil bath to 110-120°C while

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[#] Mfd. by FreKote, Inc., Indianapolis, Indiana.

stirring occasionally with a non porous stirrer. When the mixture was completely clear, it was deaerated in an evaporator for approximately twenty minutes. After ensuring the mixture had cooled to 80-90°C, the 5 pph by weight of curing agent was added. It was stirred until homogeneous and poured into the preheated mold.

Only two curing methods were used. The standard method was to cure at 120°C for two hours, let the mold and the oven cool slowly to at least 50°C, post cure at 130°C for two hours and then allow to cool slowly to room temperature. The other method was to cure at 74°C for four hours and allow to cool slowly to room temperature. The plates were then masked with masking tape to preserve the smooth surface (The earlier specimens were polished in a polishing jig).

Machining of the specimens was accomplished using a band saw and a small milling machine. Strips of material approximately $\frac{1}{2}$ inch wide and three inches long were cut from the cast plates. The edges were milled parallel to a width of 0.375 inches and then the fillet was cut with a 9/32 inch end mill. A cutter with a 0.006 inch tooth radius was used to notch the earlier specimens. The holes in the holed ones were drilled using a jig and a 0.0635 (#52) inch diameter drill.

Thesis 118363
L8922 Ludwig
Deformation bands
in thermoset polymers.

2[illegible] SEP 70 DISPLAY

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